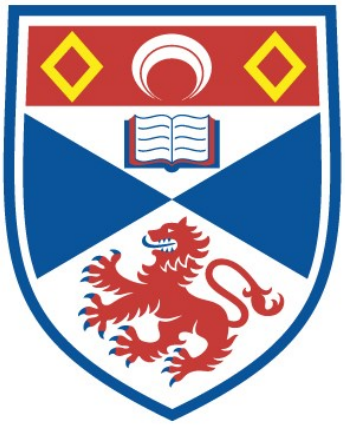
SOME NEW HETEROCYCLIC THERMOSETS

Neil James Nicolson

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1996

Some New Heterocyclic Thermosets

A thesis by

Neil James Nicolson

submitted for the degree of Doctor of Philosophy in the Faculty of Science of the University of St. Andrews

April 1996

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Declaration

I, Neil James Nicolson, hereby certify that this thesis has been composed by me, that it is an accurate representation of the work undertaken by me in the University of St. Andrews since my admission as a Research Student on 1st October 1992, and that it has not been accepted in any previous application for any Higher Degree or professional qualification.

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I hereby certify that Neil James Nicolson has fulfilled the Regulations appropriate to the Degree of Ph.D.

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Dedication

This thesis is dedicated to my Mum, Dad and Grandparents.

Contents

Acknowledgements

I would like to express my gratitude to Dr. David Smith for getting me to this stage through his supervision, help and encouragement.

I am also indebted to ICI and to the School of Chemistry for the funding of the project. My special thanks go to Drs. P.T. McGrail, P.D. MacKenzie and C.I. Lindsay, and Mr. W.S. Dewar of ICI, and I also acknowledge the help I have received from Messrs. J.T. Carter, G. Emmerson and S. Quinn during the time I have spent at ICI's Wilton laboratories.

Thanks are also due to the following St. Andrews staff: Mr.J.S.G. Smith for help with DSC, Mr.C. Millar for mass spectra and Mrs. S. Williamson for the microanalysis.

Finally, I would like to thank all the people with whom I have had the fortune (or perhaps misfortune!) to share a lab over the past few years for their sometime willing assistance, good company and stimulating (!) conversation.

Abstract

The original aim of this project was to investigate the possibility of synthesising a novel polymer system combining the best features of cyanate ester resins and epoxy resins. Chapter 1 presents the historical background for both types of resin.

The remaining three chapters describe attempts to achieve this aim by a) finding a cyanate ester that cures at a lower temperature than those in current commercial use (Chapter 2); b) using mixed epoxy and cyanate ester resins (Chapter 3); and c) designing chemically completely novel polymers from knowledge of the existing ones (Chapter 4).

In Chapter 2 it was revealed that different cyanate esters cure at different temperatures, but that no obvious correlation exists between curing temperature and either steric or electronic effects of the ring substituents. The mixing of two dicyanate esters, one of which cures at a lower temperature than the other, leads to some reduction in the overall curing temperature required, but not sufficient to warrant further study at this stage.

In Chapter 3 the usefulness of a previously proposed co-reaction between cyanate esters and epoxides was examined. Previous work in this area is full of inconsistencies that put many of the proposed conclusions in doubt. Further examination of the alleged co-reaction reveals that any such co-reaction is unpredictable, can vary significantly with reaction conditions and is in any case a minor reaction pathway by comparison with the self-reactions of the two individual reactants. It was therefore decided that further pursuit of this strategy was also likely to prove unrewarding in the short term.

In Chapter 4 a study was made into the effects of including novel monomers in a standard epoxy resin system. These novel monomers had a cyanurate backbone with epoxide functionality, and can be cured at the lower temperatures of epoxy resins. Tests on the properties (mechanical, dielectric, water absorption, fracture toughness etc.) of these polymers were of a preliminary "scouting" nature, but are sufficiently promising to encourage further study.

CHAPTER 1

INTRODUCTION

1.1 Historical background of high-performance organic polymers

A typical definition of a high-performance organic polymer is one which retains useful properties after thousands of hours of exposure at 200°C in air under static conditions. However, it has been pointed out[1] that this definition can be misleading and varies considerably depending on the supplier and the user. Commonly temperature is reported without regard to other influential factors which affect the performance of a polymer. These factors include: the time it is subjected to the particular temperature; thermal cycling (i.e. the repetitive heating and cooling of a material, for example a satellite moving in and out of the Earth's shadow); stress and environmental factors like moisture, chemical or electrical action. Furthermore, polymers that are processed at high temperatures but subsequently not exposed to them, are also referred to as high-temperature or high-performance polymers.

It was in the late 1950s that the search for high-performance organic polymers began, stimulated by the requirements of the relatively new aerospace and electronics industries. In the aerospace industry the main uses for these polymers are as substitutes for metals as a result of their improved strength to weight ratio. In the electronics industry they are used mainly as insulating materials in printed circuit boards. These industries still provide the driving force for research into new improved high-performance organic polymers although many other applications[1,2,3], as listed below, are currently in use or are being considered, depending on the precise properties of the polymer:

- Ablators (thermal protection systems)
- Adhesives

- Aircraft structures
- Automotive components
- Civil engineering
- Coatings
- Cryogenic tanks
- Electronic and microelectronic components
- Flooring
- Gaskets, sealants, tubing and pipes
- Household items
- Insulating materials
- Jet engines
- Medical devices
- Missiles and rockets
- Nuclear reactor components
- Radomes and antennae
- Satellite and space structures
- Stealth and low observables (radar invisible materials)
- Tooling, casting and moulding.

This is a very extensive range of applications and by no means the limit, so it is easy to see why further research into high-performance organic polymers is justified.

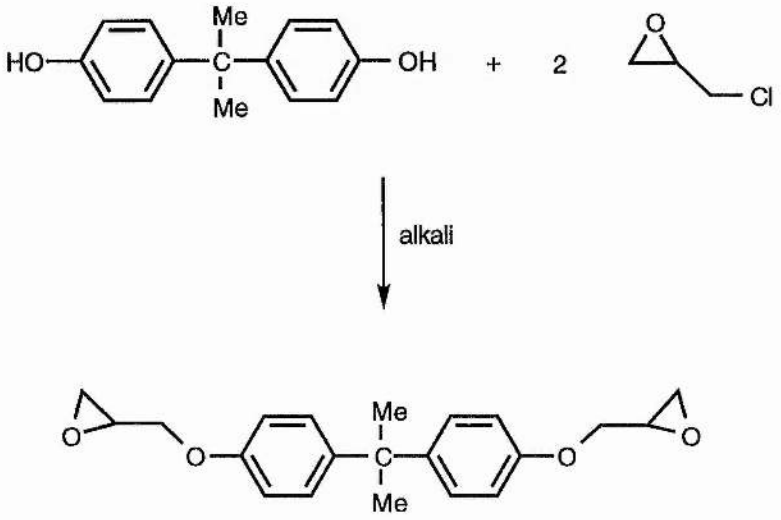
The field of high-performance organic polymers includes a number of polymer types including some aromatic thermoplastics, e.g. poly(ether ether ketones) and poly(ether sulfones), but mainly thermosetting polymers, e.g. polyimides and epoxy resins. The most commonly used systems in the major applications to date are epoxy resins. For example, in the aerospace industry in 1987, epoxy resins made up the matrix in over 90% of structural composites.[2]

1.2 Epoxy resins

1.2.1 Background

What would now be called epoxy resins were first synthesised as early as 1891[3]. However, it was not until the 1940s that epoxy resins became commercially available. These early epoxy resin monomers were the reaction products of bisphenol A and epichlorohydrin, as shown in Fig.1.1 below.

Fig.1.1



Although there are many other types of epoxy resins available, the above reaction still provides most of the currently marketed monomers.

For successful application of epoxy resins it is necessary to react the diepoxide with a suitable curing agent (or hardener) and then cure the resin to attain a controlled network structure, detailed in section 1.2.3.

1.2.2 Curing agents

A curing agent is used to convert epoxy monomers to hard, infusible thermosetting networks by the promotion of cross-linking. This can occur by either homopolymerisation initiated by a catalytic agent or a polyaddition / copolymerisation reaction with a multifunctional curing agent (see section 1.2.3). The selection of curing agents is very wide, as shown by Table 1.1[3] which lists the estimated relative world market usage in 1989 for the commercially most significant curing agent types.

Table 1.1

Curing agent type	Relative use (%)
Amines	22
Polyamides	16
Polyamidoamines	7
Phenol- and amino-formaldehyde resins	16
Carboxylic acid terminated polyesters	22
Anhydrides	12
Polysulfides and polymercaptans	3
Other catalysts	2

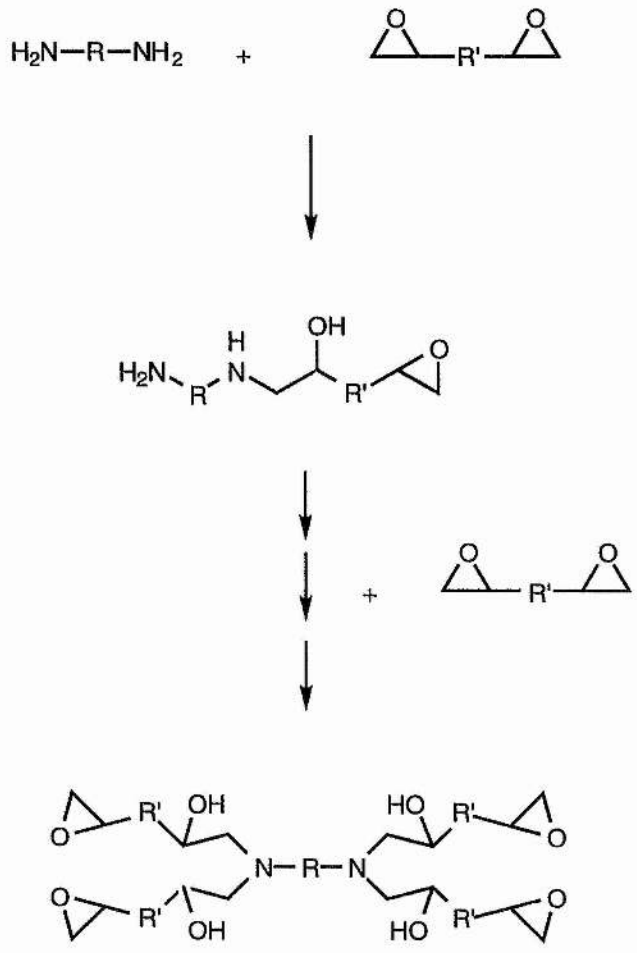
The precise choice of curing agent depends on the specific ultimate requirements of the polymer, as the nature of the curing agent as well as the epoxy monomer itself has an effect on the properties of the polymer.

1.2.3 Amine curing reactions

Amines are amongst the best studied and most commonly used curing agents[4]. They can be used in one of two ways.

Primary and secondary amines react directly with epoxide monomers (Fig. 1.2).

Fig. 1.2

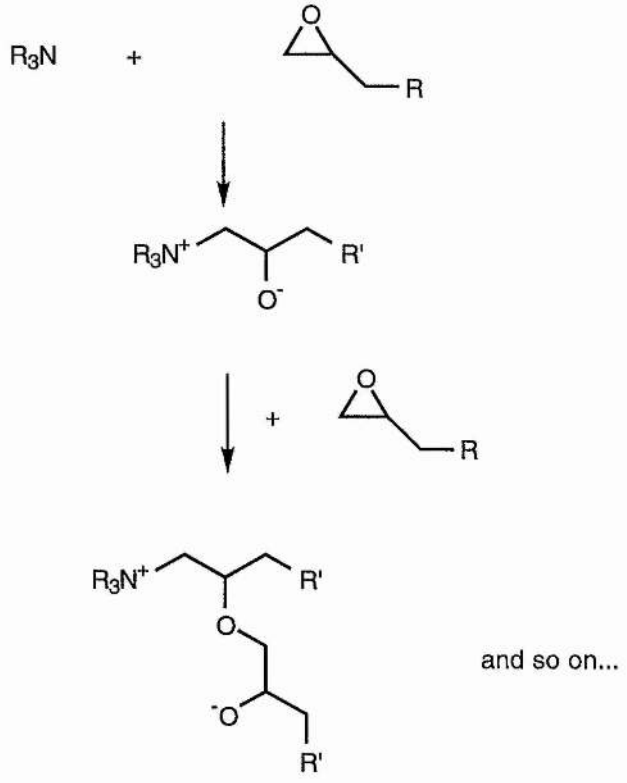


With further reaction with more diamine and diepoxide leading to extension in a linear fashion.

For thorough cross-linking in this manner the number of amine hydrogens should be matched 1:1 with the number of epoxy groups. However the alcohol produced by the ring opening can itself act to extend the chain length further by nucleophilic ring-opening of the epoxide, and therefore the proportions of monomers do not necessarily need to be stoichiometric.

Alternatively tertiary amines can be used in a catalytic manner to initiate a self-perpetuating anionic polymerisation (Fig. 1.3).

Fig. 1.3



1.2.4 Properties of cured epoxy resins

Epoxy resins have long been the choice for a wide variety of applications because of their many desirable properties. First and foremost is their good mechanical

performance which endows them with strength and toughness. Another important factor, which is in fact favourable in all thermosetting resin systems, is that the polymerisation is an addition reaction with no production of volatiles. Production of gases leads to cavities being formed in the cured polymer and hence decreases strength. Epoxy resins have good low-temperature properties, which are important in space applications, and are hot melt filmable, which means that they are relatively easy to process.

However, epoxy resins are by no means perfect and do suffer from a number of important undesirable properties. High moisture uptake leads to problems with moisture expansion and hygrostrain and the upper service temperature limit may be reduced significantly in a moist environment due to the lowering of the glass transition temperature. They also have a propensity to microcrack, a problem which is partly overcome by deliberately microcracking the material before it is used so that all the deformations can be accounted for. If microcracking happens whilst the material is being employed there is nothing that can be done about it. Another disadvantage is that epoxy resins have a low cure minimum viscosity, which means that the material is "runny" before it cures which in turn leads to wastage when material is lost from the mould. Furthermore, in composites, this can lead to the polymer not being evenly distributed through the fibres but concentrated in some areas and deficient in others. In addition, epoxy resins have relatively high dielectric constants, a property which limits their use in the electronics industry.

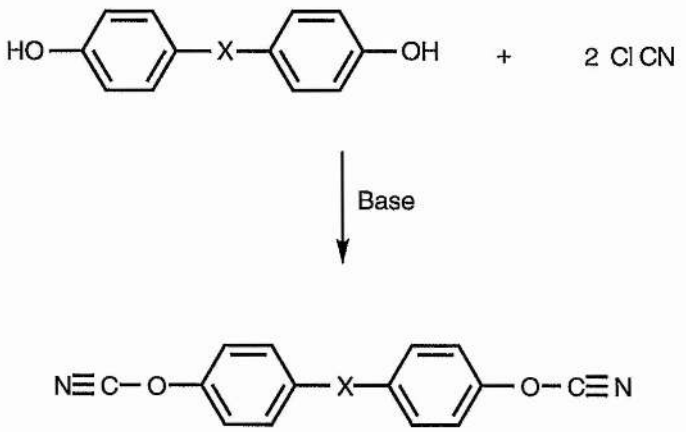
Together these properties mean that epoxy resins are the favoured option for many applications where the material is not exposed to particularly harsh conditions. However, for the increasing number of applications where severe conditions are experienced, higher performance polymers are needed.

1.3 Cyanate ester resins

1.3.1 Background

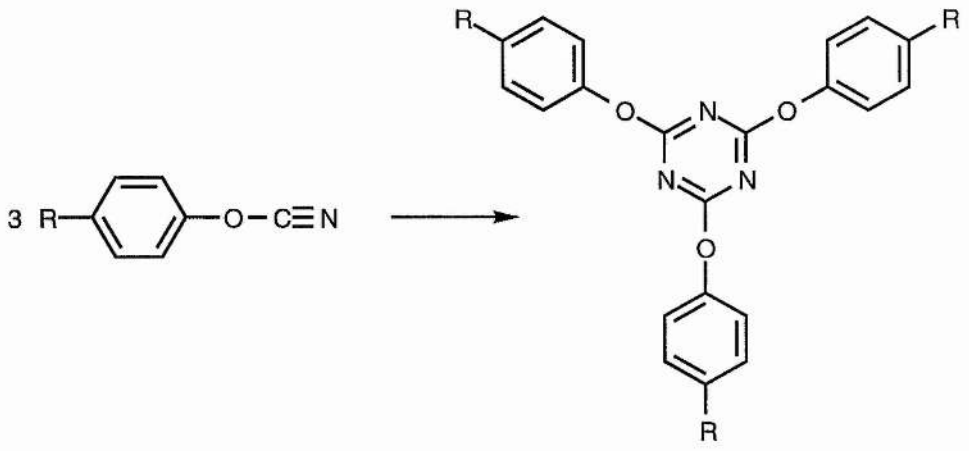
Recently the interest in cyanate ester resins as a replacement for epoxy resins, for other existing materials, and indeed for new applications, has grown rapidly. Aryl cyanates are a class of compound first synthesised in the 1960s (see Chapter 2 - Cyanate Esters), and the first commercial polymers based on these came out in the late 1970s. Cyanate ester monomers are commercially synthesised by the reaction of a bisphenol with cyanogen chloride in the presence of a base (Fig. 1.4).

Fig. 1.4



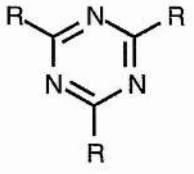
Cyanate esters are quite reactive and can trimerise easily to 1,3,5-triazines[5] on heating or in the presence of acidic or basic impurities (Fig. 1.5).

Fig. 1.5

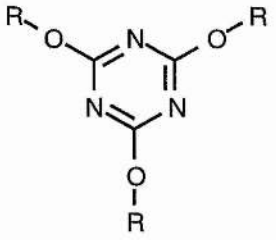


These trialkoxy- or trisaryloxy-1,3,5-triazines are sometimes referred to as trialkyl or triaryl cyanurates: the term cyanurate includes the linking oxygen atoms, as illustrated in Fig. 1.6 below.

Fig. 1.6



1,3,5-triazine



cyanurate

1.3.2 Curing reactions

Fig. 1.7

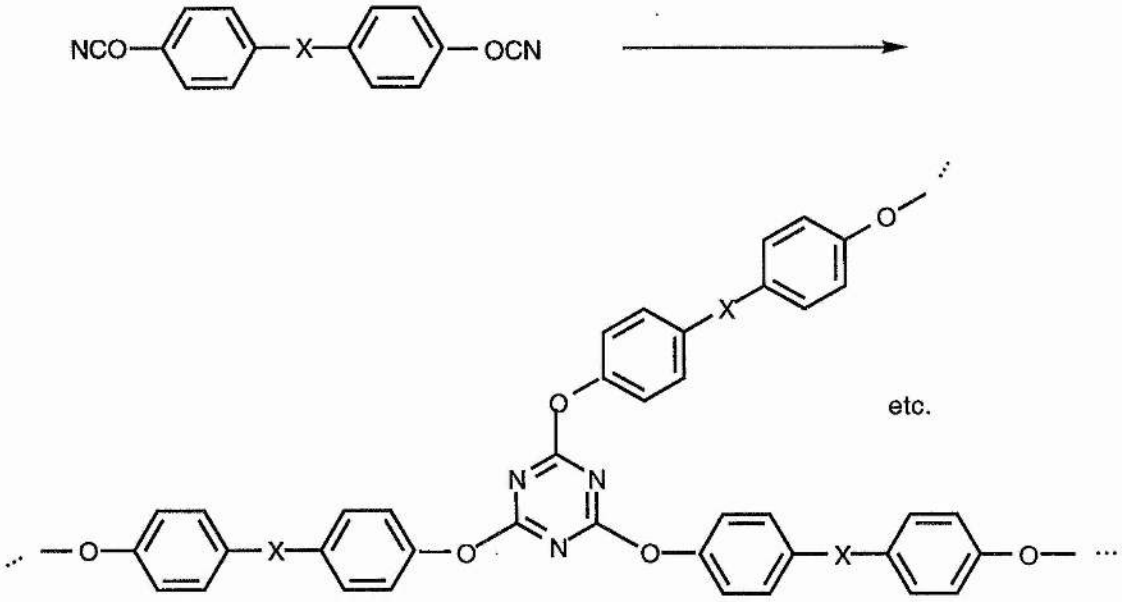


Fig. 1.7, above, shows how application of the trimerisation reaction to bifunctional cyanate esters leads to the formation of a highly cross-linked network. Three cyanate ester groups trimerise in an apparently stepwise fashion[6] to give the 1,3,5-triazines. This formation of the triazine rings is the mechanism by which cross-linking is achieved.

The trimerisation reaction can be initiated by heat only, but more practically is catalysed by a mixture of a transition metal complex and a weak acid, e.g. copper (II) acetylacetonate in nonylphenol.[7]

1.3.3 Properties of cured cyanate ester resins

To become worthwhile commercial products, cyanate ester resins have to show improved properties over what is currently available. As it has already been stated that epoxy resins are the most commonly used polymers for the major applications

(aerospace and electronics industries), cyanate ester resins must be able to outperform them in order to be considered as attractive alternatives.

Cyanate ester resins have comparable properties to epoxy resins in a number of areas. Again there is no production of void-inducing volatiles in their preparation. They have good mechanical performance with generally higher glass transition temperatures, therefore higher service temperatures. They also have good low temperature properties and they are hot melt filmable.

But they also have significantly improved properties in other areas, namely, a lower moisture uptake, improved microcrack resistance, a less wasteful higher cure minimum viscosity, lower dielectric constant and good radiation resistance, this last property being another important factor in space applications.

These properties can be correlated with structural features of a cured cyanate ester resin.[7] Fig. 1.7 shows such a resin where X can be one of a number of groups. The single atom ring linkages help to keep the T_g high (typically in the range 250-290°C) and introduce a degree of flame retardancy. Also, the balanced dipoles (the electropositive triazine carbons being surrounded by electronegative nitrogen and oxygen atoms) and the absence of strong hydrogen bonding lead to the low dielectric constant, the low melting points of the monomers and low moisture absorption.

However, cyanate ester resins suffer from one major disadvantage with respect to epoxy resins: a higher cure temperature is necessary. This means that more residual stresses are built into the polymer during curing, and, significantly, the energy costs for production are higher.

1.4 Novel resin systems

1.4.1 Necessity for an alternative resin

Potentially cyanate ester resins have the improved properties relative to epoxy resins that would make them an attractive replacement for the latter, and would also open up new applications. For example, in aircraft structural composites it would be better if they did not absorb water, as this can lead to deformations and can limit performance until the water has been removed by evaporation. Also, in insulation of electronic printed circuits, a material with a low dielectric constant and associated low electrical dissipation factor would be preferable, and again cyanate ester resins have the advantage over epoxy resins in this respect. However, the brittleness and higher curing temperature of cyanate ester resins mean that wholesale replacement of epoxy resins with cyanate ester resins is not viable.

What is needed is some kind of compromise system which incorporates the best features of both resin types and eliminates the drawbacks. Three possible strategies towards these ends are:

1 - To find a cyanate ester that cures at a lower temperature.

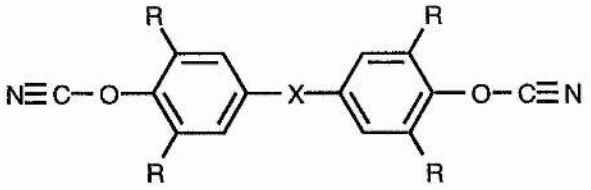
2 - To use mixed epoxy and cyanate ester resins.

3 - To find a way to design chemically such a polymer from knowledge of the existing ones.

1.4.2 Previous work in these areas

Work to find "lower curing" cyanate esters has concentrated on varying the chemical functionality of the monomers. A general structure for cyanate ester monomers is shown in Fig. 1.8 below.

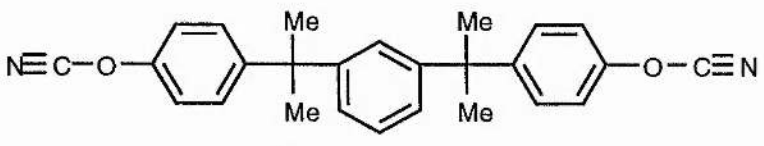
Fig. 1.8



The most commonly used cyanate ester is based on bisphenol A (R=H and X=CMe_2 in the above structure), although other compounds involve additional substituent groups (R≠H) and alternative linking groups X. It has also been noted that if the link X consists of a tetrahedral carbon atom carrying two different substituents then this tends to cause depression of the melting point and can lead to more easily handled liquid monomers[7].

The standard curing temperature for cyanate esters is 177°C (350°F) with further post-curing at >200°C necessary to ensure complete conversion. The aim is to find cyanate esters which will cure at lower temperatures, ideally down to 121°C (250°F). A developmental cyanate ester has been designed with this in mind[8] (Fig. 1.9), but the properties of the polymer formed from this monomer are poorer than when the curing is carried out at higher temperatures, and, in general, significantly poorer than those of other cyanate esters cured at these higher temperatures. This is due to a conversion of cyanate ester groups to triazines of <85%, although it should be noted that for a cure temperature of 121°C, 85% is still much higher than usual.

Fig. 1.9



This shows how altering the chemical nature of the cyanate ester can affect the curing temperature, and that the topic is worth further investigation.

At present cyanate esters are quite often mixed with epoxy resins to obtain materials of sufficient toughness for particular applications. In these mixtures there is homopolymerisation of both monomers as well as a degree of co-reaction between cyanate ester and epoxide. This co-reaction is complicated, and various reaction schemes have been proposed.[9-16] These schemes are very different, but do propose oxazolidinone or oxazoline final products.

These schemes are discussed further in Chapter 3, but there is little doubt that this reaction needs further investigation, and its importance is diminished by the facts that the degree of co-reaction is very limited and is apparently subject to wide variation by processing conditions. For these reasons it was felt that an alternative way of combining cyanate ester and epoxide systems by much more predictable chemistry was necessary: this is described in Chapter 4.

While this work was in progress, Fyfe *et al.* published work along similar lines using a mixed functionality monomer to link covalently cyanate ester and epoxy resins.[17] This involved using a compound with both cyanate ester and epoxy functionalities, and is also described in Chapter 4.

1.4.3 Intended work

At the outset of the project, it was considered that further work was needed on all these approaches, in order to find a system which incorporates the best features from both epoxy resins and cyanate ester resins. The following chapters will describe our work in each area and will explain in more detail the rationale behind the experimental work and the background not already discussed. The topics are as follows: "lower-curing" cyanate esters; epoxy and cyanate ester co-reactions; and novel polymers in which triazine functionality is incorporated into epoxy resins.

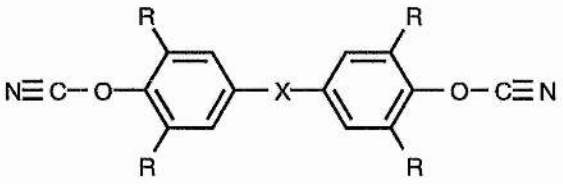
CHAPTER 2

CYANATE ESTERS

2.1 Introduction

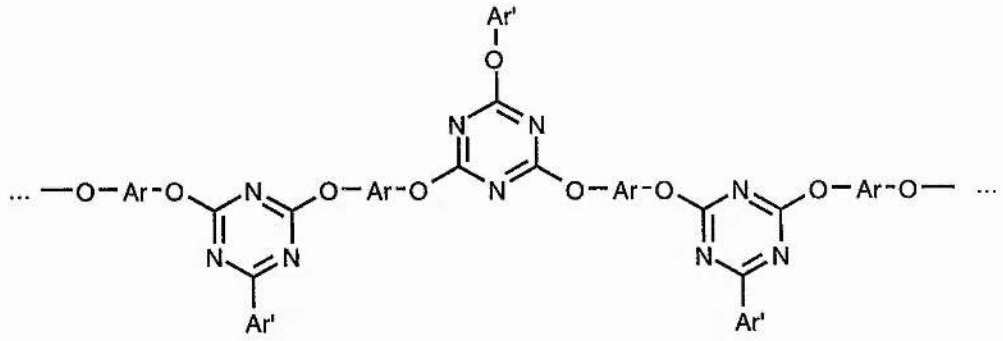
There is the possibility that the use of different cyanate esters may lead to the discovery of one which cures at a lower temperature, but maintains the beneficial properties of a cyanate ester resin, compared with an epoxy resin. This means the variation of group X (see Fig. 2.1), the possible addition of side groups (R≠H) and also the use of different length cyanate esters (i.e. a different number of atoms between the cyanate groups) so as the distance between the cyanate ester functionalities can be varied. "Longer" cyanate esters would lead to a larger distance between the cyanurate rings in a polymer, hence reducing the cross-link density and changing the properties of the polymer.

Fig. 2.1



Another option is to co-polymerise dicyanate esters with monocyanate esters. Increasing the proportion of monocyanate ester to dicyanate ester would decrease the cross-linking possibly even to the extent that the material would become a thermoplastic, as illustrated below (Fig. 2.2).

Fig. 2.2



However, this could also produce some trimer of the monocyanate ester as well as polymer, which is not desirable as it introduces an unpolymerised impurity.

Blending of different dicyanate esters is one further option worthy of investigation.

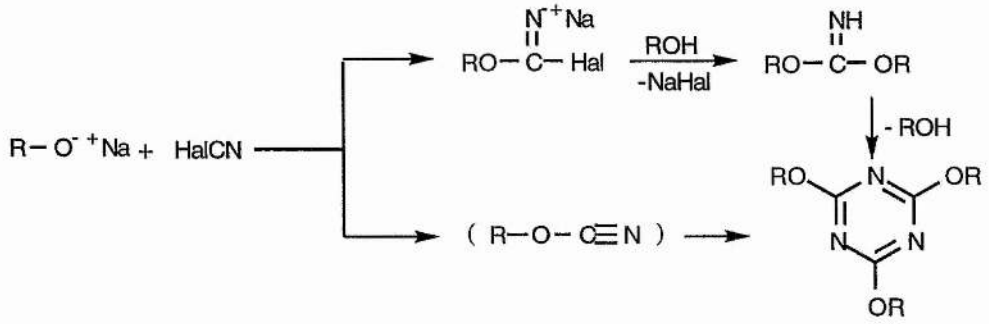
To investigate these possibilities many different cyanate esters have to be synthesised, and therefore a reliable method of synthesis is required.

Only relatively recently have the first true cyanate esters (cyanates ROCN) been synthesised because the cyanate ion was always alkylated through the nitrogen to give the iso form[18] (isocyanates OCNR) (Fig. 2.3).

Fig. 2.3

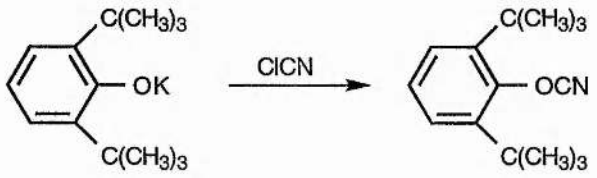
Attempts were made to synthesise cyanate esters as early as the second half of the nineteenth century by reaction of phenoxides (or alkoxides) with cyanogen halides. This was first done in 1857 by Cloez[19], nearly ten years after isocyanates were discovered. Cyanate esters were never isolated and the main reaction products were tri-alkoxy-1,3,5-triazines (trialkyl cyanurates) and imidocarbonates formed in a reaction scheme (Fig. 2.4) worked out by Hantzsch and Mai[20] and Nef[21] in 1895.

Fig. 2.4



The first cyanate esters were produced by Stroh and Gerber[22] in 1960 by a similar method. These were made from sterically hindered *o*-substituted phenols (Fig. 2.5).

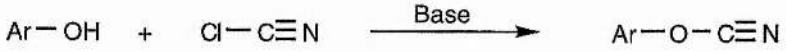
Fig. 2.5



In this case the cyanate ester does not react further to give the cyanurate or imidocarbonate, presumably because of the steric hindrance.

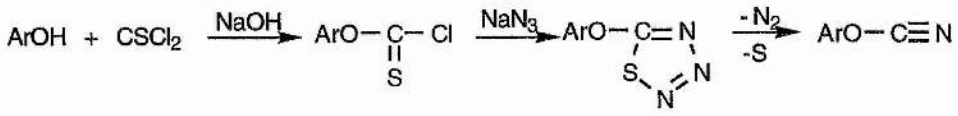
The major breakthrough (in terms of a general synthesis of cyanate esters) was achieved in 1963 by Grigat and Pütter at Bayer AG in Germany[23,24]. They discovered a simple synthesis (Fig. 2.6) of cyanate esters by the reaction of phenols with cyanogen halides in the presence of an appropriate base, e.g. triethylamine (avoiding an excess of phenoxide). This method is successful with mono- and poly-phenols and can easily be carried out on an industrial scale with excellent yields.

Fig. 2.6



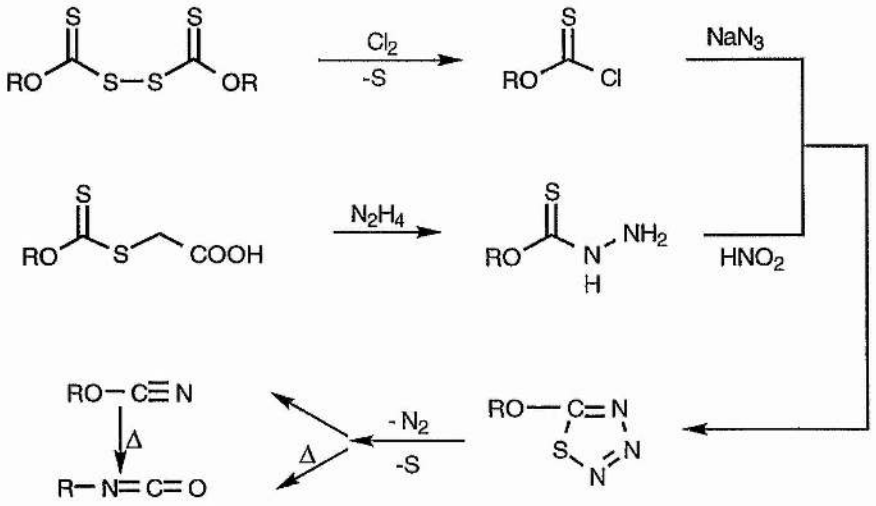
Around the same time two other methods were reported. Martin in Berlin[25,26] obtained aromatic and then aliphatic cyanate esters by the thermolysis of 1,2,3,4-thiatriazoles (Fig. 2.7).

Fig. 2.7



Jensen and Holm[27] in Copenhagen used a similar method, but using different starting materials (Fig. 2.8).

Fig. 2.8



A number of other methods for the synthesis of cyanate esters have been described in the literature[28-33], but they suffer from disadvantages such as a large number of stages and low yields and so are not very promising for practical purposes.

For this research we decided to use Grigat and Pütter's method because it involves the least number of steps, gives the highest yields and is the industrially used route to most commercially available cyanate esters.

For details on the industrial synthesis of cyanate ester monomers see ref. 34.

2.2 Results & Discussion

2.2.1 Synthesis of cyanate esters

Phenyl cyanate proved difficult to make. The first attempt resulted in the production of the impure phenyl cyanate which when distilled under vacuum for purification produced some white solid. Over a few days all of the purified liquid turned into the solid which was found to be triphenyl cyanurate. Triethylamine is named as a reagent which promotes the trimerisation of phenyl cyanate[24], so perhaps a little of this is still present and the temperature of distillation causes trimerisation without the need for a separate trimerisation reaction. However on a repetition of the reaction the trimer was formed even before distillation and could be recrystallised from the original reaction mixture. An authentic sample of triphenyl cyanurate was made from cyanuric chloride and phenol for comparison purposes, and indeed the two samples were identical (m.p., I.R., n.m.r.). It seems that phenyl cyanate is difficult to make because it is a liquid and therefore its purification (by distillation) requires the application of heat.

An improved method[35] was then used which employed different mole ratios and column chromatography as the means of purification. This method yielded phenyl cyanate as a stable colourless liquid.

p-Chlorophenyl cyanate is a solid, and indeed it can be made much more easily than the non-halogenated version. However purification is difficult because it trimerises on attempted recrystallisation. This problem can again be overcome by the use of column chromatography as the purification technique.

The next cyanate ester to be synthesised was 2,6-dimethylphenyl cyanate for the reason that the two methyl groups cause steric hindrance around the cyanate group and make it less likely to trimerise. ^{13}C n.m.r. spectroscopy shows that the product isolated from the reaction mixture is very pure cyanate but the fact that it is an acute lachrymator

shows that it is still highly reactive. Recrystallisation is again not possible but in this case not necessary.

Characterisation of the cyanate esters was achieved by ^{13}C n.m.r. and I.R. spectroscopy as well as mass spectroscopy and melting point measurement. The cyanate carbon has a characteristic chemical shift of ~108-110 ppm and the ring carbon to which the cyanate group is attached has a chemical shift of ~151-155 ppm. Ring carbons in the triazine ring have a shift of ~174 ppm. The presence of a C≡N absorption at ~2250 cm^{-1} in the I.R. spectrum is indicative of the preparation of a cyanate ester, as is the C-O-C absorption at 1235-1160 cm^{-1}. Absorption at 1580 cm^{-1} shows the presence of a C=N bond in a conjugated heteroaromatic system (i.e. a triazine).

The dicyanate esters chosen for the initial study were those derived from readily available diols. 2,2-Bis(4-cyanatophenyl)propane is a commercially available dicyanate ester and its derived polymer resin is used in an industrially made composite. Therefore it was used as a standard for spectral characterisation and for working out the best synthetic route. A sample was made from bisphenol A and cyanogen bromide which had identical characteristics to those of the commercial sample.

4,4'-Dicyanatodiphenyl sulphone is also available commercially but only as a monomer/polymer mixture. When the preparation of this dicyanate ester was attempted the reaction product was found also to be a monomer/polymer mixture (a brittle lump of orange solid). By conducting the reaction under conditions of increased dilution the amount of polymerisation could be reduced (although not entirely) so that the appearance of the product was a light orange coloured powder.

The preparation of other dicyanate esters was also carried out with the reasoning that changing the chemical nature and geometry of the central group as well as varying

the length of the dicyanate ester would have an effect on the properties of any polymer incorporating them.

1,4-Dicyanatobenzene is the simplest aromatic dicyanate ester and can readily be prepared and purified without any sign of polymerisation.

4,4'-Dicyanatobiphenyl can also be prepared easily and can be used as a standard to help determine the effect of a central group between the two rings as it does not have one.

1,1,1,3,3,3-Hexafluoro-2,2-bis(4-cyanatophenyl)propane was chosen as a halogenated analogue of the 2,2-bis(4-cyanatophenyl)propane to investigate the effect of a halogen-containing dicyanate ester. This product was obtained initially as a monomer / polymer mixture but column chromatography provides a means of purification.

[1,1-Bis(4-cyanatophenyl)ethyl]benzene, bis-(4-cyanato-3,5-dimethylphenyl)methane and 9,9-bis(4-cyanatophenyl)fluorene have all been successfully prepared but again prove difficult to purify. Column chromatography once more is necessary for full purification. These dicyanate esters have been chosen as representative monomers containing an unsymmetrical central group, sterically hindered cyanate groups and a bulky central group respectively.

In order to study the effect of a "longer" dicyanate ester, 4,4'-bis(*p*-cyanatobenzoyl)biphenyl was synthesised. In this compound the geometry is also changed by having trigonal carbonyl groups linking the aromatic rings, rather than the tetrahedral central groups in the previous molecules. This compound shows the correct I.R. spectrum, but solid state n.m.r. is necessary on account of very low solubility.

This very low solubility means that purification has so far proved impossible as both recrystallisation and column chromatography are impracticable.

The most interesting results of these experiments are that there does not seem to be any direct correlation between structure and reactivity of these dicyanate esters. The ease with which they undergo polymerisation is not apparently dependent on whether the central group donates or withdraws electrons. This then poses the following question: what does control which of the dicyanate esters polymerise prematurely and which do not?

There is obviously a need for a more systematic way to define the relative reactivities of cyanate esters than merely to observe their tendency to polymerise on attempted purification. To do this differential scanning calorimetry (D.S.C.) was used to provide values for curing temperatures. D.S.C. has been used previously to measure enthalpies of reaction but apparently not for curing temperatures, the main drive of this chapter.

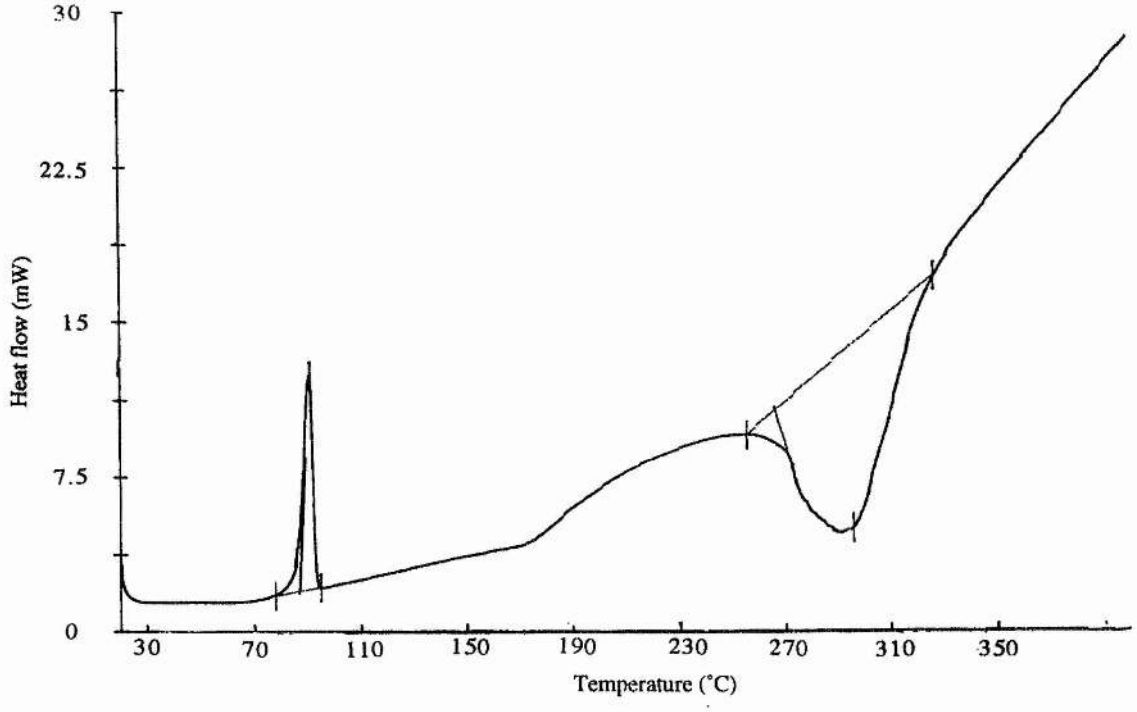
2.2.2 Cure temperatures

The following figures show D.S.C. scans of the dicyanate esters synthesised.

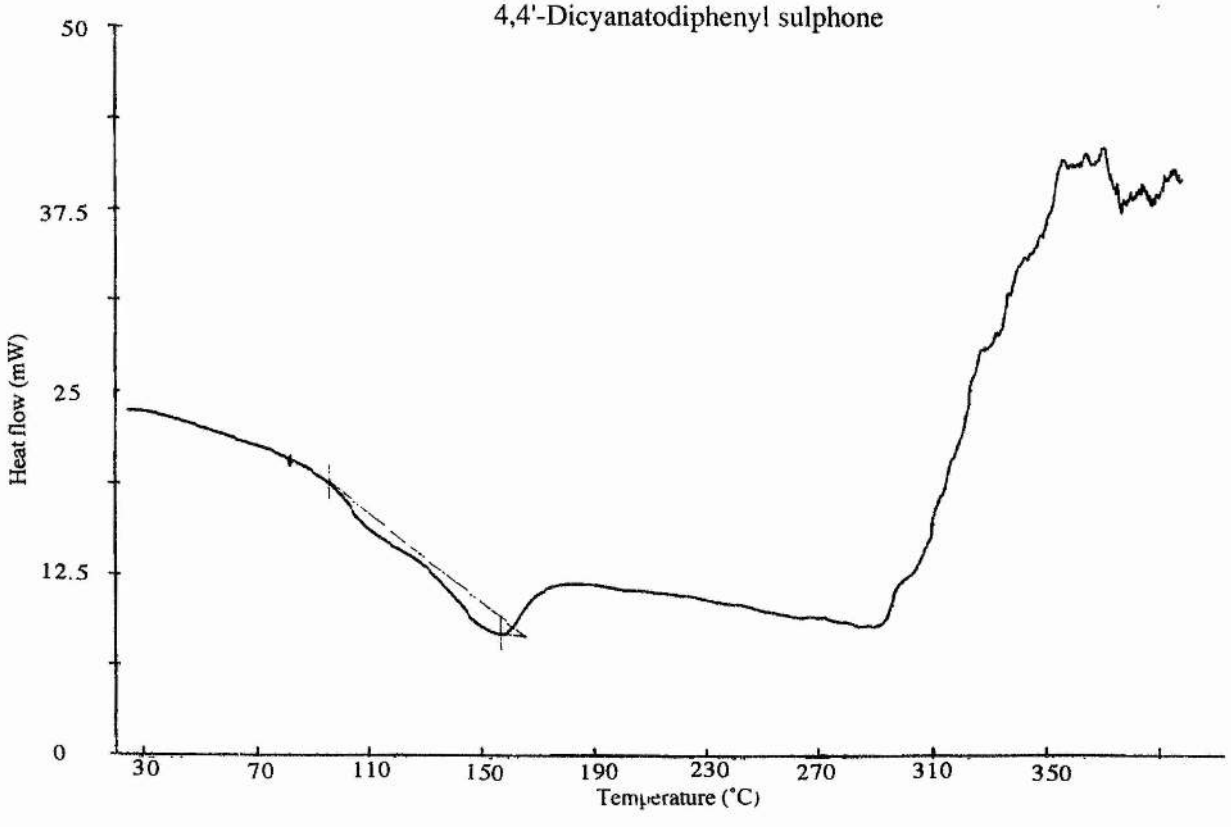
In the scans the upward peaks are melting point endotherms and the cure temperature is taken as the onset of the rather broader exotherms. These cure temperatures are listed in Table 2.1 (below).

It can be seen that neither 4,4'-dicyanatodiphenyl sulphone or 4,4'-bis(*p*-cyanato-benzoyl)biphenyl show melting point endotherms. This is consistent with there being no visually observed melting point in either case.

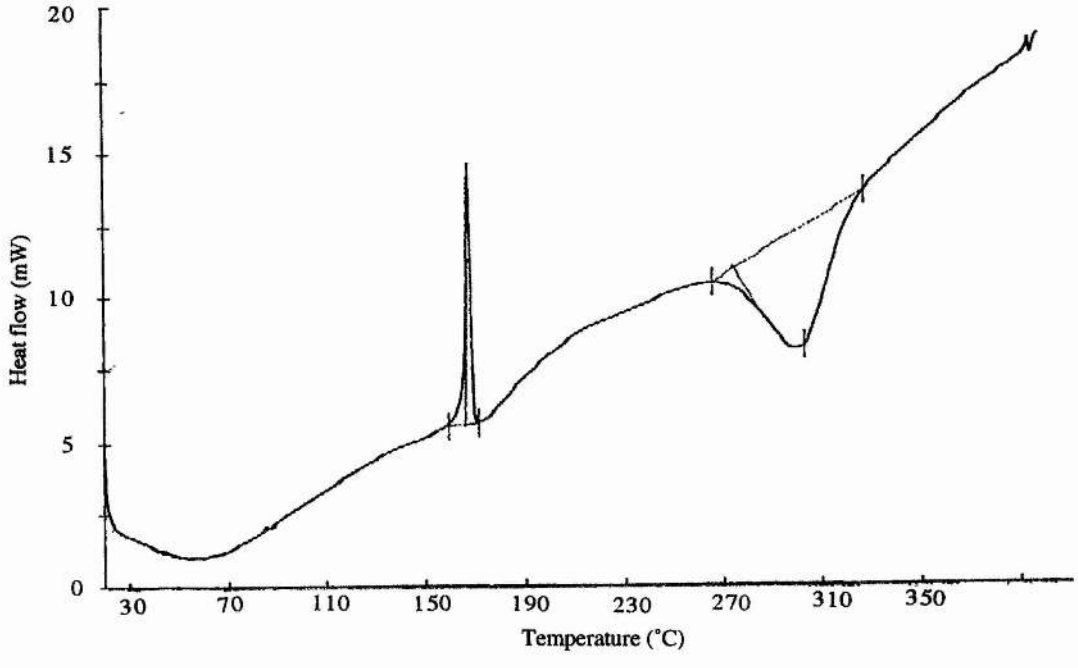
[1,1-Bis(4-cyanatophenyl)ethyl]benzene



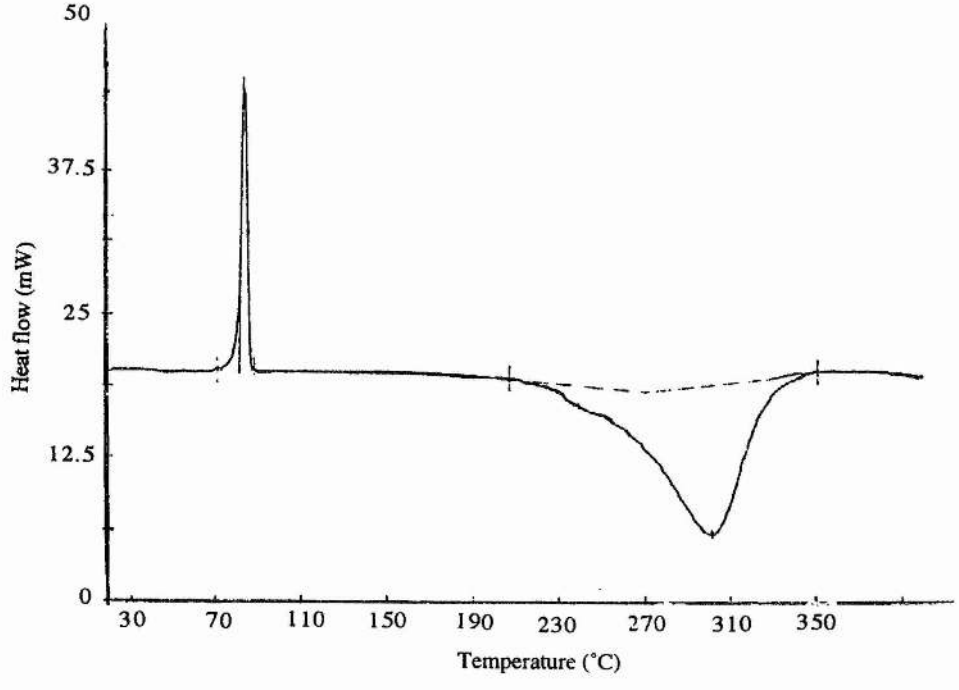
4,4'-Dicyanatodiphenyl sulphone



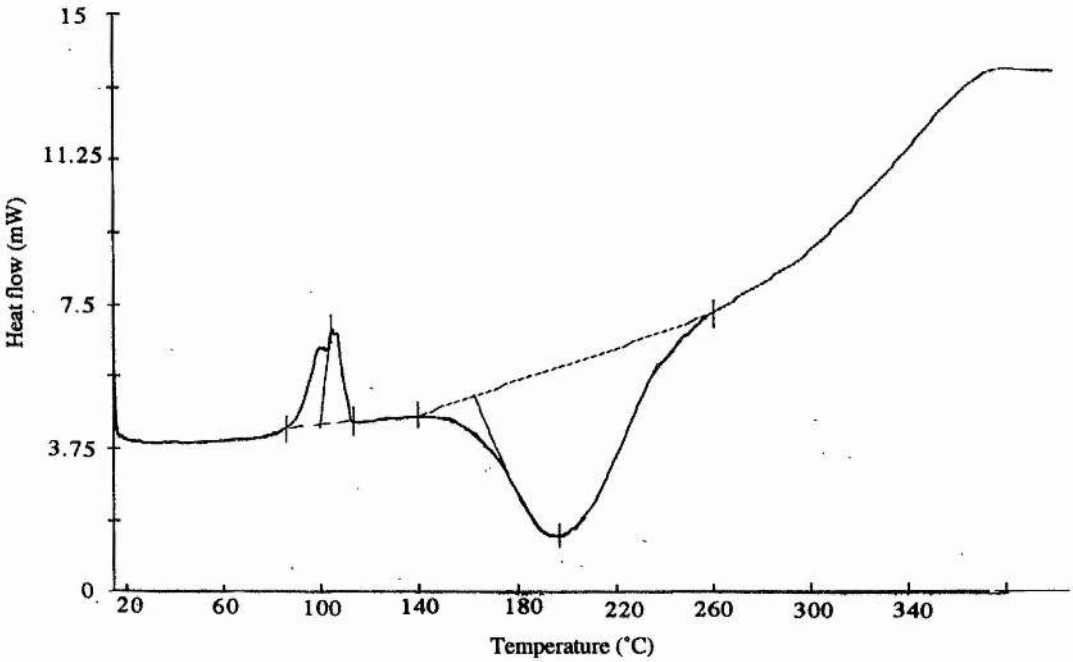
9,9-Bis(4-cyanatophenyl)fluorene



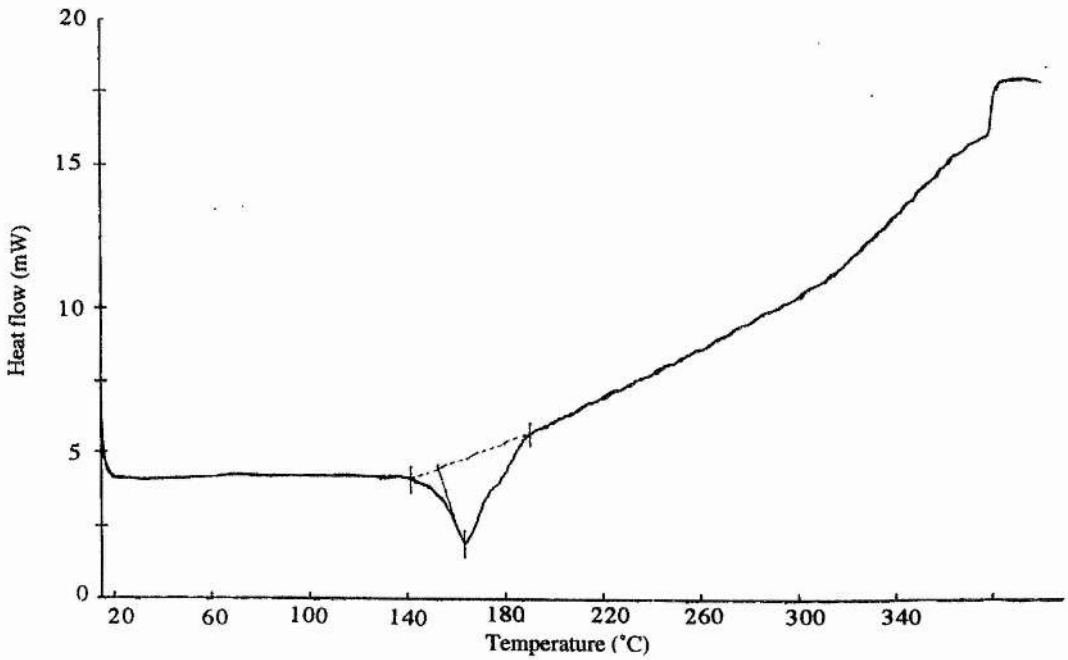
2,2-Bis(4-cyanatophenyl)propane



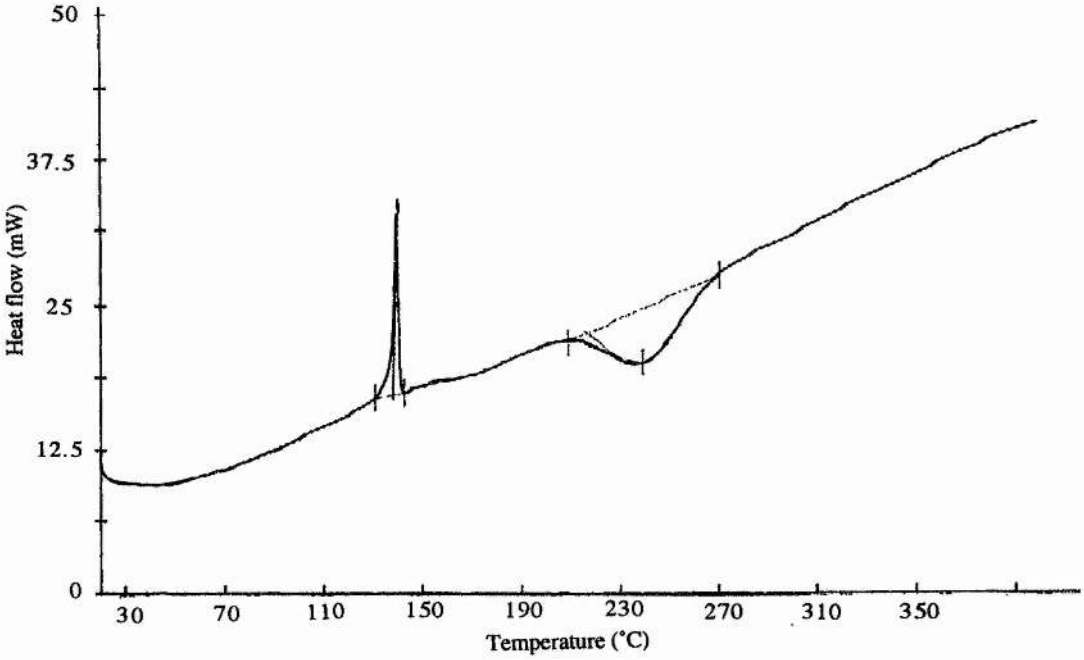
1,4-Dicyanatobenzene



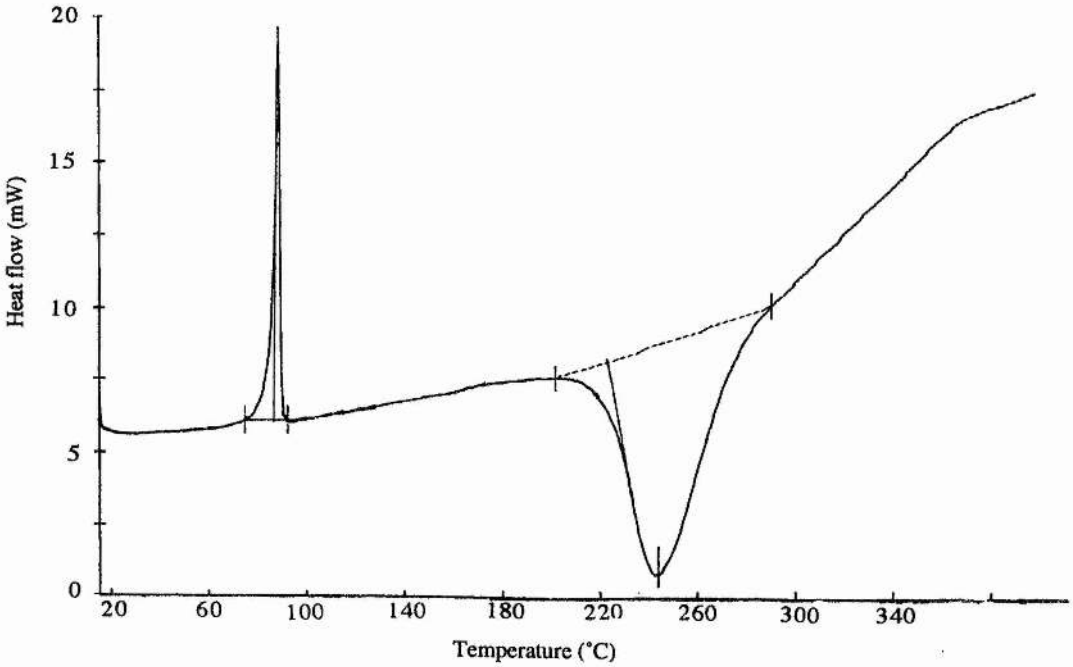
4,4'-Bis(*p*-cyanatobenzoyl)biphenyl



4,4'-Dicyanatobiphenyl



1,1,1,3,3,3-Hexafluoro-2,2-bis(4-cyanatophenyl)propane



Bis-(4-cyanato-3,5-dimethylphenyl)methane

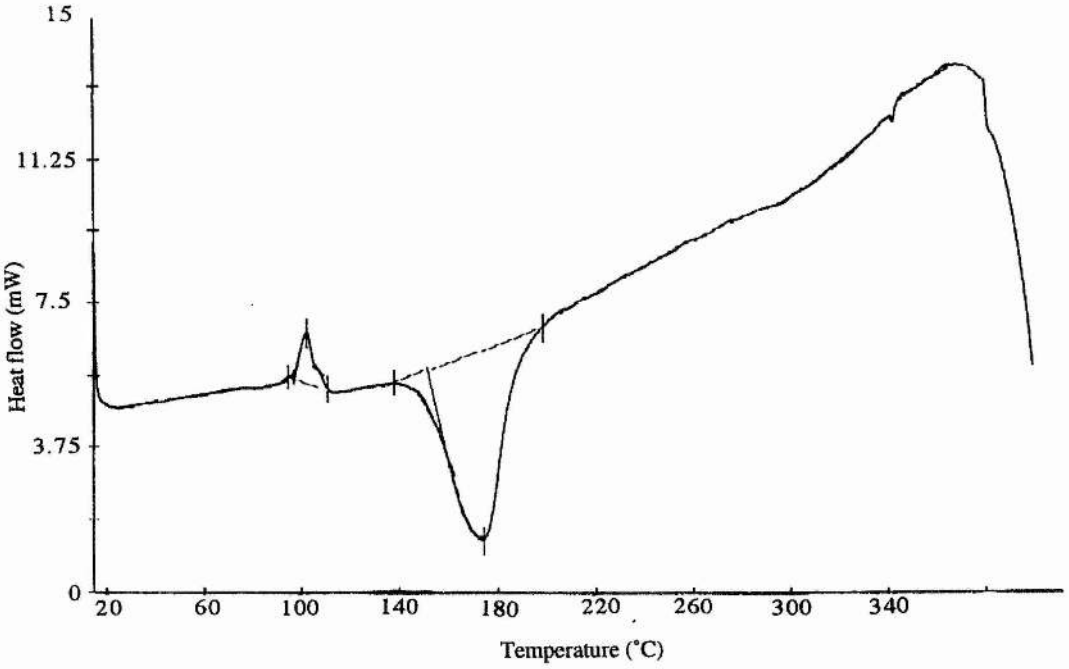


Table 2.1

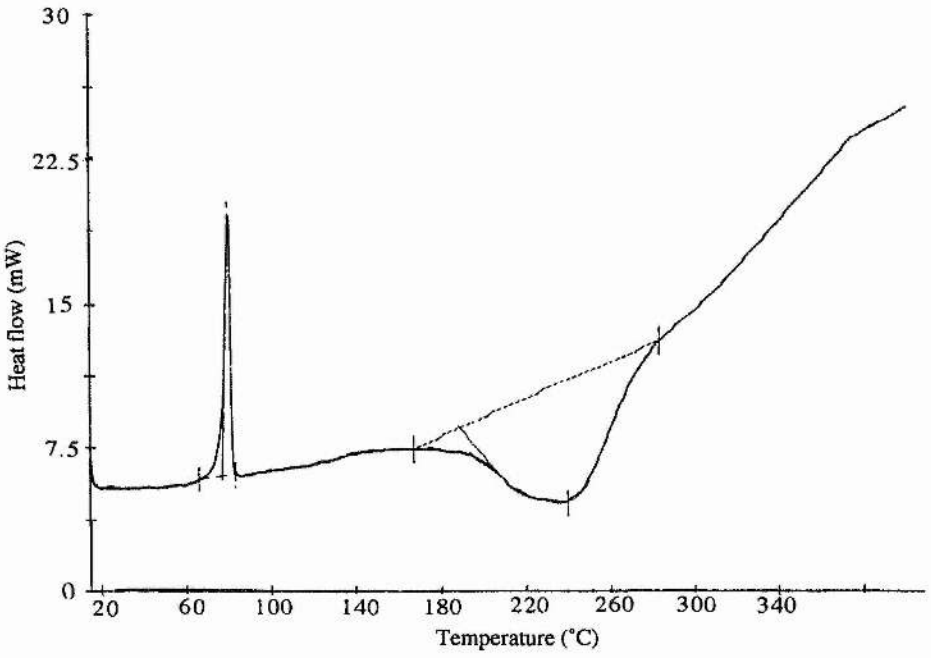
Cyanate ester	Cure temperature (°C)
[1,1-Bis(4-cyanatophenyl)ethyl]benzene	255
4,4'-Dicyanatodiphenyl sulphone	80
9,9-Bis(4-cyanatophenyl)fluorene	266
2,2-Bis(4-cyanatophenyl)propane	207
1,4-Dicyanatobenzene	139
4,4'-Bis(*p*-cyanatobenzoyl)biphenyl	141
4,4'-Dicyanatobiphenyl	209
1,1,1,3,3,3-Hexafluoro-2,2-bis(4-cyanatophenyl)propane	201
Bis-(4-cyanato-3,5-dimethylphenyl)methane	138

These results confirm that there is still no obvious correlation between curing temperature and either steric or electronic effects of the ring substituents.

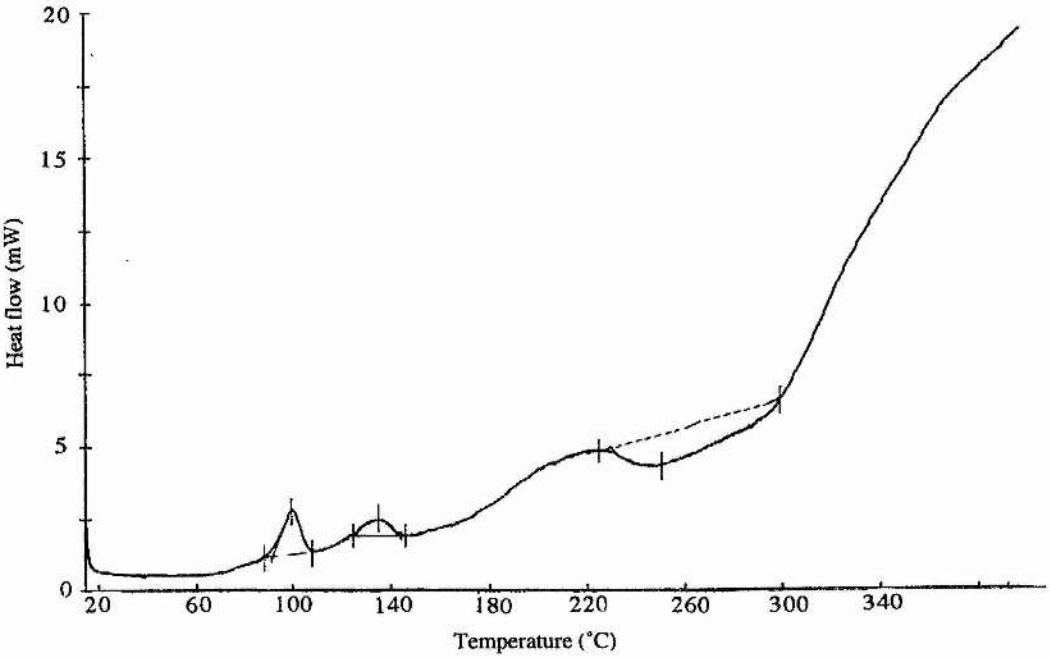
Another possible approach to achieve low temperature curing might be to employ a mixture of dicyanate esters, in the hope that the heat given off as the lower-curing dicyanate ester cures may initiate a co-reaction of the two dicyanate esters or the curing of the other dicyanate ester at a lower temperature than normal.

The following two D.S.C. scans show the results of such experiments. It can be seen that a small amount of 4,4'-dicyanatodiphenyl sulphone does start the curing of 2,2-bis(4-cyanatophenyl)propane at a slightly lower temperature than usual. Similarly, curing of the 1:1 mixture of 1,4-dicyanatobenzene and 9,9-bis(4-cyanatophenyl)-fluorene begins at a slightly lower temperature than that of the latter (more thermally stable) component on its own, but there is no obvious sign of the self-curing of the dicyanatobenzene at the expected temperature. These preliminary experiments were not considered sufficiently encouraging to warrant further study at this stage and attention was concentrated instead on possible cyanate ester / epoxide co-reactions.

4,4'-Dicyanatodiphenyl sulphone and 2,2-bis(4-cyanatophenyl)propane (1:5)



1,4-Dicyanatobenzene and 9,9-bis(4-cyanatophenyl)fluorene (1:1)



2.3 Experimental

Triphenyl cyanurate from cyanuric chloride[19]

Cyanuric chloride (9.22 g, 0.05 mol) was heated with a small excess of phenol (16.9 g, 0.18 mol) at 185-210°C for 5 h under reflux. The mixture was then extracted with boiling methanol and the product recrystallised from dioxan: m.p. 224-226°C (lit.[18] 235-236°C). Yield 9.05 g (50%).

Tris-(*p*-chlorophenyl) cyanurate from cyanuric chloride

This was obtained as above from cyanuric chloride (4.61 g, 0.025 mol) and *p*-chlorophenol (11.56 g, 0.09 mol). M.p. 202-206°C (lit.[36] 200-205°C); yield 7.39 g (64%).

Cyanates from phenols - Method A

This is the original method of Grigat and Pütter[24] except that cyanogen bromide was used instead of cyanogen chloride due to availability and relative ease of handling. A solution of the phenol (x mol) in Analar acetone was cooled to 0°C and added to cyanogen bromide ($1.05x$ mol). Then triethylamine (x mol) was added dropwise under ice cooling and vigorous stirring so that the temperature did not exceed 10°C. After the addition was complete the mixture was stirred for a further 10 minutes. The precipitated triethylamine hydrobromide was removed by filtration. The residue was washed three times with acetone and was then rejected. The acetone and any remaining cyanogen bromide were removed under reduced pressure. The product was then distilled if it was a liquid or recrystallised if it was a solid.

Cyanates from phenols - Method B

This is a modified version of Method A.

The phenol (x mol) was dissolved in acetone and under ice/salt cooling cyanogen bromide ($1.05\ x$ mol) was added. Triethylamine (x mol) was added dropwise so that

the temperature did not rise significantly. Triethylamine hydrobromide was precipitated as the reaction progressed. After 15 minutes' further stirring the mixture was added, with good stirring, to copious amounts of ice-water, and the cyanate was isolated by filtration and recrystallised.

In the case of diols cyanogen bromide (2.1 *x* mol) and triethylamine (2 *x* mol) were used.

Cyanates from phenols - Method C

This is a version of Method B used when the product does not precipitate out on addition of water sufficiently to allow filtration. In these cases the product was extracted with dichloromethane, and the extract dried with magnesium sulphate and concentrated under reduced pressure.

Cyanates from phenols - Method D

This method is adapted from a more recent paper[35] and involves different mole ratios and a different purification procedure.

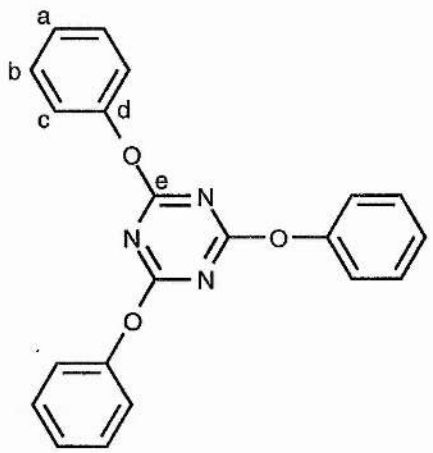
The phenol (*x* mol) was dissolved in acetone and under dry ice / acetone cooling cyanogen bromide (1.4*x* mol) was added. Triethylamine (1.4*x* mol) was added dropwise over 1 h with vigorous stirring. The mixture was then allowed to warm up to room temperature over 1.5 h before being poured into water. It was then extracted with dichloromethane, the extract dried over magnesium sulphate and the solvent evaporated under reduced pressure. The crude product was then purified by column chromatography on silica gel with eluant an 80:20 mixture of dichloromethane and petroleum (b.p.40-60°C). The cyanate was rapidly eluted whilst the impurities were strongly adsorbed on the column.

In the case of diols the amounts of cyanogen bromide and triethylamine were doubled to 2.8 *x* mol.

Phenyl cyanate (2)

Method A was used with phenol (9.41 g, 0.1 mol) in acetone (25 cm^3). As it was distilled (b.p. 70°C / 12 mmHg) the phenyl cyanate was converted into its solid white trimer. Triphenyl cyanurate (1) had m.p. 229-230°C (from acetic acid; lit.[36] 225°C).

Fig. 2.9



(1)

^{13}C n.m.r.($CDCl_3$ / TMS) (refers to carbon atoms labelled in Fig. 2.9) .

C-atom	a	b	c	d	e
δ/ppm	126.0	129.4	121.4	151.6	173.7

Mass spectrum: *m/z* 264 [2%, $(M\text{-}C_6H_5O)^+$], 214 [33], 170 [15], 141 [29], 119 [16, $C_6H_5OCN^{+\cdot}$], 94 [100, $C_6H_5OH^{+\cdot}$], 77 [87, $C_6H_5^+$], etc. The molecular ion (expected at *m/z* 357) is absent.

The I.R. spectrum shows a distinctive peak at 1570 cm^{-1} which appears to be characteristic of a triazine ring system.

This experiment was repeated with the same conditions and the trimer formed spontaneously in the reaction mixture without the need for distillation.

Method D was then used with phenol (6.3 g, 0.066 mol) and acetone (100 cm^3) as solvent. The product was a colourless liquid with a strong infra-red absorption at 2250 cm^{-1}, indicating the presence of the cyanate group. Yield 7.53 g (94%).

For ^{13}C n.m.r. see Table 2.2.

_p_-Chlorophenyl cyanate (3)

Method B was used with *p*-chlorophenol (12.8 g, 0.1 mol) and acetone (250 cm^3) as solvent. The crude product has m.p. 36-37°C (lit.[37] m.p. 42°C). Yield 12.45 g (81%). The product has a C≡N absorption at 2250 cm^{-1} in the I.R.

It is not pure enough to give a clean ^{13}C n.m.r. spectrum but the characteristic peak for the cyanate carbon is present at ~108 ppm. Attempted recrystallisation gives a compound which has m.p. 207-209°C (from methanol) and is identical to tris(*p*-chlorophenyl)triazine (*cf.* p.31).

Method D was used with *p*-chlorophenol (8.48 g, 0.066 mol) and acetone (100 cm^3) as solvent. This gives a pure product m.p. 36-37°C (lit.[37] 42°C). Yield 9.16 g (90%).

For ^{13}C n.m.r. see Table 2.2.

2,6-Dimethylphenyl cyanate (4)

Method B was used with 2,6-xylenol (12.2 g, 0.1 mol) and acetone (250 cm^3) as solvent. The crude product (yield 6.07 g, 41%) has m.p. 34-35°C (lit.[37] m.p. 38°C).

The crude product has not been recrystallised due to very high solubility and low melting point. However a ^{13}C n.m.r. spectrum has been obtained with no sign of any impurities (see Table 2.2). In the I.R. spectrum a C≡N absorption is also present at 2250 cm^{-1}.

Method D was used with 2,6-xylenol (8.05 g, 0.066 mol) and acetone (100 cm^3) as solvent. This gave a pure product with m.p. 33-35°C (lit.[37] 38°C) and yield 8.03 g (83%).

For ^{13}C n.m.r. results see Table 2.2.

4,4'-Dicyanatodiphenyl sulphone (5)

Method A was used with bisphenol S (12.4 g, 0.05 mol) as the phenol and acetone (25 cm^3). After the acetone was removed the product was an orange brittle solid of polymeric nature (as confirmed by I.R. and ^{13}C n.m.r.).

The reaction was repeated and gave the same product.

Another repetition was done, removing the acetone without any heating (in case warming caused the polymerisation), but there was no further success.

A different approach was obviously needed so method B was tried. The same amount of bisphenol S was used but extra acetone was added (60 cm^3). This time the product was not orange polymeric solid but beads of pale orange colour; I.R. spectrum shows bands at 1580 cm^{-1} (C=N in a triazine ring, i.e. polymer) and 2250 cm^{-1} (C≡N).

The literature melting point of the dicyanate is 169-170°C[37]. The product obtained does not melt there, but darkens in colour (presumably polymerises) at ~290°C.

This material was most likely a mixture of dicyanate and polymer. The greater dilution probably means there is less chance of polymerisation.

The reaction was again repeated this time with 110 cm^3 acetone. The product was whiter (less polymer was formed) and darkened at ~280°C.

For ^{13}C n.m.r. results see Table 2.2.

1,4-Dicyanatobenzene (6)

Method B was used with quinol (5.51 g, 0.05 mol) and acetone (60cm^3). The m.p. was 110-111°C (lit. 115-116°C)[37]. Yield 7.18 g, (90%).

The I.R. spectrum shows strong C≡N absorption at 2270 cm^{-1} but not any carbon-nitrogen triazine absorption band, showing that polymerisation had not occurred.

For ^{13}C n.m.r. see Table 2.2.

Method D was also used with quinol (3.63 g, 0.033 mol) and acetone (100 cm^3) as solvent. This gave a product with the same m.p. as that from method B but with a decreased yield, 3.68 g (70%).

2,2-Bis(4-cyanatophenyl)propane (7)

Method B was used with bisphenol A (11.4 g, 0.05 mol) and acetone (100 cm^3). The product was recrystallised from petroleum (b.p. 40-60°C); m.p. 76-77°C (lit.[37] 82°C). Yield 6.6 g, (47%).

I.R. shows the C≡N peak at 2240 cm^{-1} and also a small carbon-nitrogen (triazine) peak at 1580 cm^{-1} suggesting that a little polymer may be present.

For ^{13}C n.m.r. see Table 2.2.

Method D was used with bisphenol A (7.5 g, 0.033 mol) and acetone (100 cm^3) as solvent. The product had a slightly higher m.p. than that from method B (77-78°C) and a higher yield, 7.80 g, (86%).

4,4'-Dicyanatobiphenyl (8)

Method B was used with one-third quantities (because 4,4'-biphenol is not very soluble in acetone): biphenol (3.1 g, 0.0165 mol), cyanogen bromide (3.7 g, 0.033 mol), triethylamine (3.4 g, 0.033 mol) and acetone (100 cm^3).

Mass spectroscopy revealed that the only product was starting material. The biphenol is not completely soluble in the volume of acetone used under these reaction conditions (~0°C) and therefore does not react.

This experiment was then repeated with a different solvent. Method B was used with biphenol (4.66 g, 0.025 mol) and THF (150 cm^3) as solvent. The product was recrystallised from 1,4-dioxan to give needle-like crystals m.p. 133-135°C (lit.[37] 131°C). Yield 3.6 g (61%).

For ^{13}C n.m.r. see Table 2.2.

1,1,1,3,3,3-Hexafluoro-2,2-bis(4-cyanatophenyl)propane (9)

Method C was used with 1,1,1,3,3,3-hexafluoro-2,2-bis(4-hydroxyphenyl) propane (1.68 g, 0.005 mol) as the phenol and acetone (150 cm^3) as solvent. The product gives a C≡N absorption band at 2250 cm^{-1} in the I.R. spectrum and no C=N

triazine absorption band. The ^{13}C n.m.r. spectrum shows there are impurities but most of the expected peaks can be identified.

Method D was used with 1,1,1,3,3,3-hexafluoro-2,2-bis(4-hydroxyphenyl) propane (3.36 g, 0.01 mol) and acetone (30 cm^3) as solvent. This gave a pure product m.p. 85-86°C (lit.[38] 87-88°C). Yield 2.89 g (75%).

For ^{13}C n.m.r. see Table 2.2.

[1,1-Bis(4-cyanatophenyl)ethyl]benzene (10)

Method C was used with bisphenol AP (2.1 g, 0.0075 mol) as the phenol and acetone (70 cm^3) as solvent. The product is a viscous liquid, obviously impure (lit.[38] m.p. 87-88°C), but does show a C≡N absorption at 2250 cm^{-1}.

Method D was used with bisphenol AP (4.2 g, 0.015 mol) and acetone (50 cm^3) as solvent to provide a pure product m.p. 82-85°C, yield 3.57g (72%).

For ^{13}C n.m.r. see Table 2.2.

Bis(4-cyanato-3,5-dimethylphenyl)methane (11)

Method C was used with tetramethyl bisphenol F (1.28 g, 0.005 mol) as the phenol and acetone (150 cm^3) as solvent. A yellow liquid was produced. This liquid, though not purified, has a large C≡N absorption at 2250 cm^{-1} in the I.R. spectrum but no C=N in a triazine ring absorption.

Method D was used with tetramethyl bisphenol F (2.56 g, 0.01 mol) and acetone (30 cm^3) as solvent. This gave a product with m.p. 103-105°C (lit.[7] 106°C). Yield 2.48 g (81%).

For ^{13}C n.m.r. see Table 2.2.

9,9-Bis(4-cyanatophenyl)fluorene (12)

Method B was used with 9,9-bis(4-hydroxyphenyl)fluorene (2.0 g, 0.006 mol) as the phenol and acetone (100 cm^3) as the solvent. The recrystallised product (acetic acid) has m.p. 161-163°C, (lit.[38] 162.5-163°C) but no cyanate absorption at 2250 cm^{-1}.

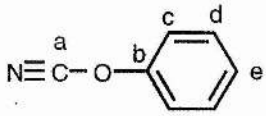
Repetition of this reaction yields a very viscous liquid which when added to diethyl ether gives a white solid. This solid does give a cyanate absorption at 2250 cm^{-1} in the I.R., but is proving difficult to purify.

Method D gave a pure product with a cyanate absorption in the I.R. and correct ^{13}C n.m.r. (Table 2.2). M.p. 166-167°C, yield 1.46 g (37%).

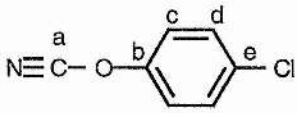
4,4'-Bis(*p*-cyanatobenzoyl)biphenyl (13)

Method B was used with 4,4'-bis(*p*-hydroxybenzoyl)biphenyl (2.5 g, 6.25×10^{-3} mol) and DMF (250 cm^{-3}) as solvent. The crude product does not melt but darkens >250°C (presumably polymerising). There is a C≡N absorption at 2250 cm^{-1} in the I.R. No ^{13}C n.m.r. data are available because of its insolubility in the normal solvents and solid state measurements do not provide much help because of the difficulty in providing a pure sample.

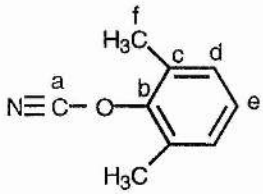
Fig. 2.10



(2)



(3)



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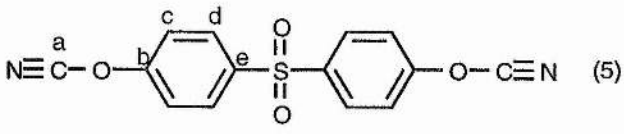
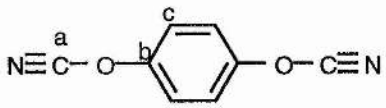
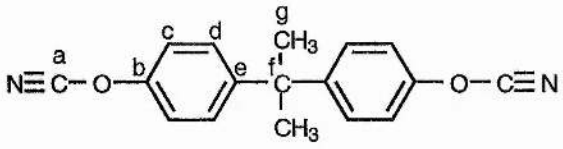


(5)

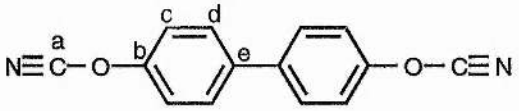
Fig. 2.10 (cont.)



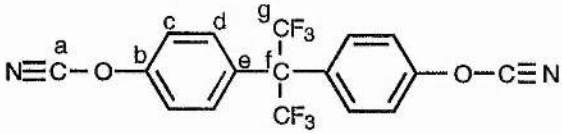
(6)



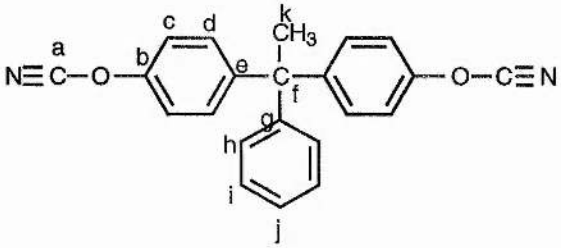
(7)



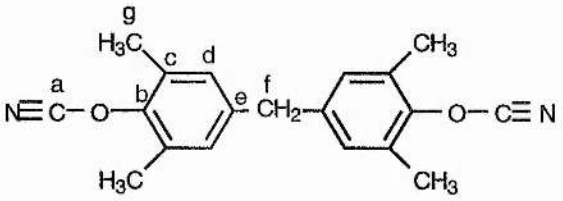
(8)



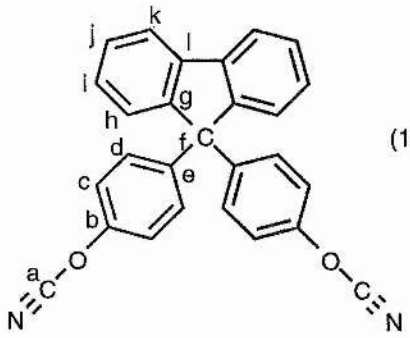
(9)



(10)

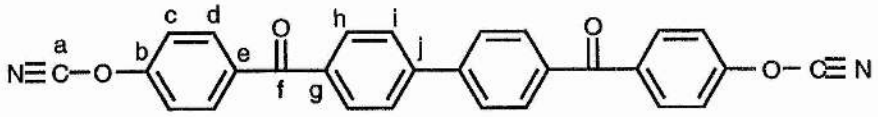


(11)



(12)

Fig. 2.10 (cont.)



(13)

Table 2.2

^{13}C n.m.r. spectra of dicyanates

(Atom labels as in Fig. 2.10)

Cpd.	a	b	c	d	e	f	g	h	i	j	k	l
(2)	109.0	153.1	115.5	130.8	127.2							
(3)	108.0	150.8	116.4	130.1	131.9							
(4)	110.1	151.0	127.4	129.4	128.4	15.3						
(5)	107.7	155.7	117.6	130.9	139.1							
(6)	108.5	151.0	118.1									
(7)	109.3	151.5	115.5	129.3	149.3	43.1	31.3					
(8)	108.2	151.5	115.4	128.4	136.6							
(9)	108.2	153.0	117.6	130.9	131.3	septet*	123.8q**					
(10)	108.0	151.2	115.1	130.7	147.4†	52.0	147.4†	128.5†	128.4†	126.9	30.8	
(11)	110.3	149.8	128.8	129.9	13.9	40.2	15.7					
(12)	108.5	151.6	115.3	129.9	144.2	64.1	149.6	120.6	128.2†	125.6	128.2†	139.9

* The septet is not visible. **J=285Hz. † Provisional assignment.

Cure temperatures

Cure temperatures were calculated using differential scanning calorimetry (D.S.C.). Samples of ~5 mg were sealed in aluminium pans and heated at a rate of 10°C per minute using a Perkin-Elmer DSC7 instrument. Cure temperatures were taken to correspond to the onset of an exotherm.

CHAPTER 3

CYANATE ESTER AND EPOXIDE CO-REACTION

3.1 Introduction

As has already been stated, the main objective of this research was to find a polymer system which has the desirable properties of a cyanate ester resin, but cures at a lower temperature like an epoxy resin. In the literature there are claims that the co-reaction of cyanate esters with epoxides has potential in this respect.

Many of these authors quote as the starting point for their research a paper by Martin[25] in *Angewandte Chemie* in 1964 which, they claim, has the first report of the reaction between a cyanate ester and an epoxide producing an oxazole structure. However, neither the original German paper nor the English translation does anything of the sort. The paper only describes the synthesis and trimerisation of phenyl cyanate, but the fallacy of its being the original reference to the co-reaction of cyanate esters and epoxides has been perpetuated so that it still appears in current papers.

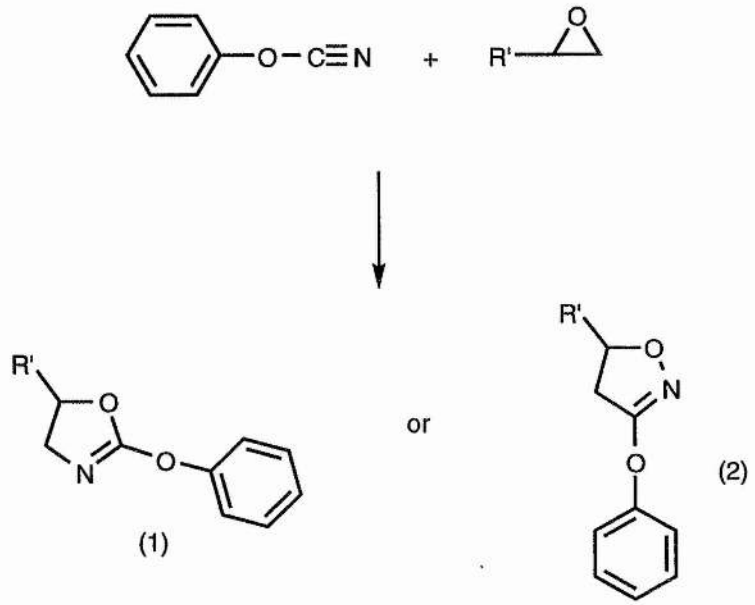
Since this fundamental error had been observed in the literature a closer examination was felt necessary. This revealed that there is considerable inconsistency between the results of different groups working in the area and a significant degree of questionable evidence upon which their conclusions are based.

The first reference to this co-reaction (other than the misquoted Martin paper[25]) is a Japanese patent[39] from 1978, the original of which was unavailable, but the summary in *Chemical Abstracts* reveals that a direct reaction of cyanate ester and epoxide groups is proposed to form an oxazoline.

More recently Gotro *et al.*[40] investigated the reaction of a bismaleimide and biscyanate ester with an epoxide, the published work being primarily concerned with the epoxide / cyanate ester co-reaction. They concluded that between 70 and 150°C

some epoxide is consumed but no reaction of the cyanate ester is observed. Then above 150°C cyclotrimerisation of the cyanate ester starts, along with competing reactions of the epoxide with the cyanate ester and epoxide homopolymerisation. A co-reaction between epoxide and cyanate ester (Fig. 3.1) is claimed on the basis of the appearance of an infra-red absorption band at 1600cm^{-1} attributed to an "iso-oxazoline" ring (*sic*), although there does not seem to be a mechanistic reason for this (Figs. 3.2 and 3.3).

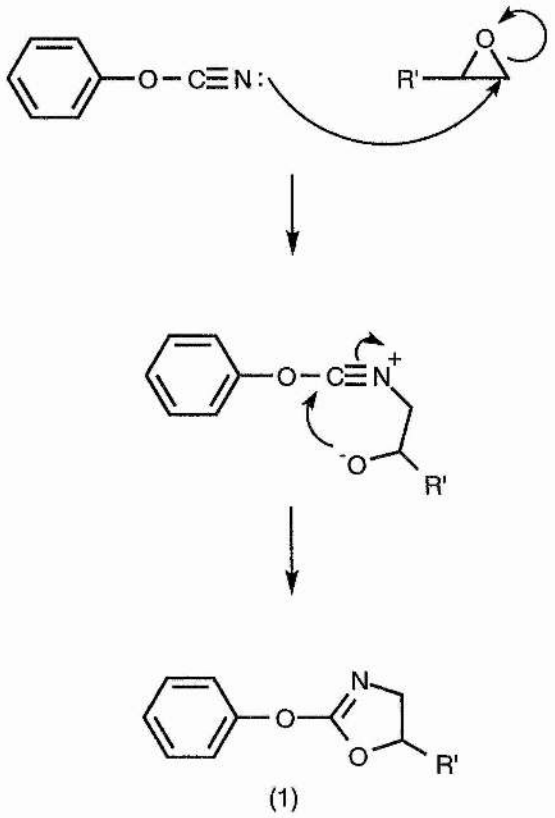
Fig. 3.1



These mechanisms (Figs. 3.2 and 3.3) show the two most likely products of this reaction, one of which is the oxazoline (1), but the other is not the isoxazoline (2), but is another oxazoline (3). The authors admit, however, that oxazoline rings have vibrations in the 1550 to 1600cm^{-1} range and all of the above peaks overlap with the "quadrant stretching" vibration of the aromatic ring (1520 to 1600cm^{-1}), and the triazine ring vibration at 1560cm^{-1}. All these possible bands occurring in the same frequency range make it very difficult to draw positive conclusions from the infra-red spectra. Also, differential scanning calorimetry shows two main reaction exotherms with others possibly hidden. The first clearly corresponds to cyanate ester trimerisation, and the

second is attributed to epoxide / cyanate ester co-reaction and epoxide homopolymerisation. These results are therefore by no means conclusive.

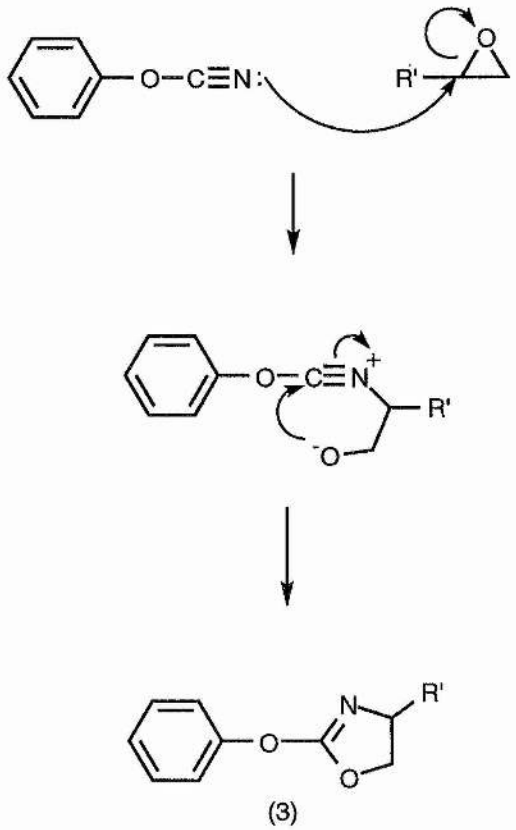
Fig. 3.2



(1)

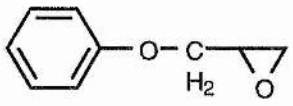
The next reference in this area is from Shimp *et al.*[14] who investigated the co-reaction of a cyanate ester and an epoxide following up on the paper by Gotro *et al.*[40] and again misquoting the Martin reference[25]. Shimp's paper claims to identify the reaction products of the co-reaction, and catalysts which promote the co-reaction. The model compounds investigated were phenyl glycidyl ether and *p*-cumylphenyl cyanate (a monofunctional analogue of bisphenol A dicyanate) as shown below (Fig. 3.4).

Fig. 3.3

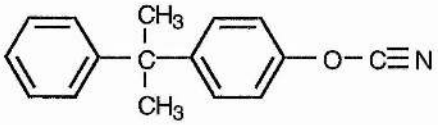


(3)

Fig. 3.4



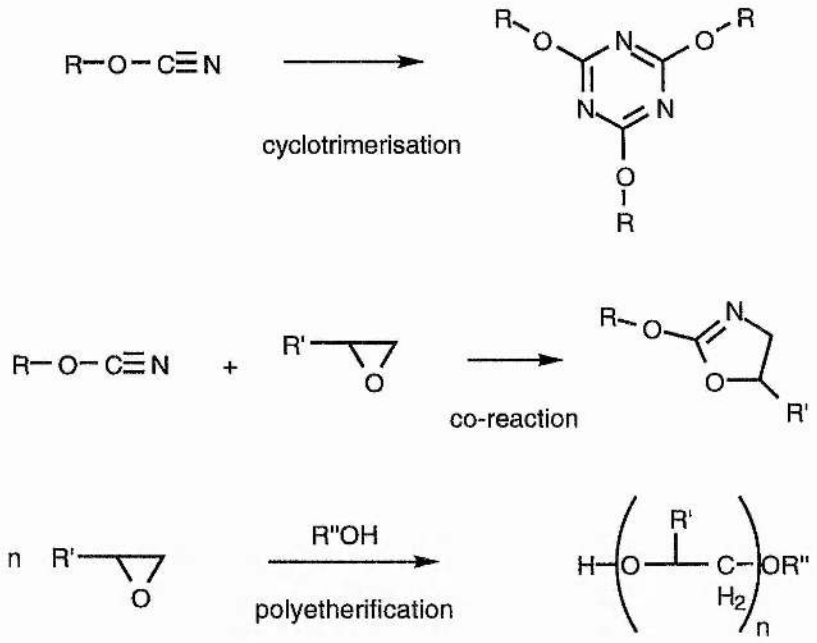
phenyl glycidyl ether



cumylphenyl cyanate

It is claimed that there are three reactions between the components of the epoxide / cyanate ester mixtures (Fig. 3.5).

Fig. 3.5



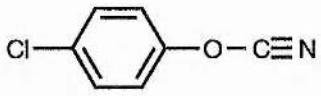
The oxazoline product (which corresponds with Gotro's oxazoline) was allegedly characterised by the appearance of three infra-red absorption bands. The peak at 1760cm^{-1} was ascribed to C-O in an imidocarbonate (an oxazoline being a cyclic imidocarbonate), but this assignment is difficult to accept since absorptions in this region are generally those of C=O or other double bond functions. Bands at 1695cm^{-1} and 1608cm^{-1} were attributed to C=N in an oxazoline and "an oxazoline ring" respectively. Reaction products were separated by gel permeation chromatography, although no spectral data are given for any of these separated products, only an infra-red spectrum of the product mixture is shown.

Also, at 60% reaction, under catalysis (precise catalyst not specified), the product mixture is quoted as consisting of 57% cyanate ester trimerisation product by weight, 26% unreacted epoxide, 13% oxazoline and 4% unreacted cyanate ester. By weight, the original reaction mixture consisted of 39% epoxide and 61% cyanate ester. Now of the

reaction products 57% cyanate ester trimerisation product plus 4% unreacted cyanate ester is 61% in total, therefore no cyanate ester is left to be incorporated into the 13% oxazoline. Furthermore, 13% of the epoxide is used up and can only be present in the oxazoline for the given group of four products. Therefore these results are not consistent with the proposed reaction scheme. These gel permeation chromatography results are more consistent with nearly all of the cyanate ester trimerising and a third of the epoxide reacting with itself (although this does not explain the infra-red results!)

Independently, at around the same time, a German research group published work in the same area[10]. This work investigated the reaction of phenyl glycidyl ether with *p*-chlorophenyl cyanate (Fig.3.6).

Fig. 3.6



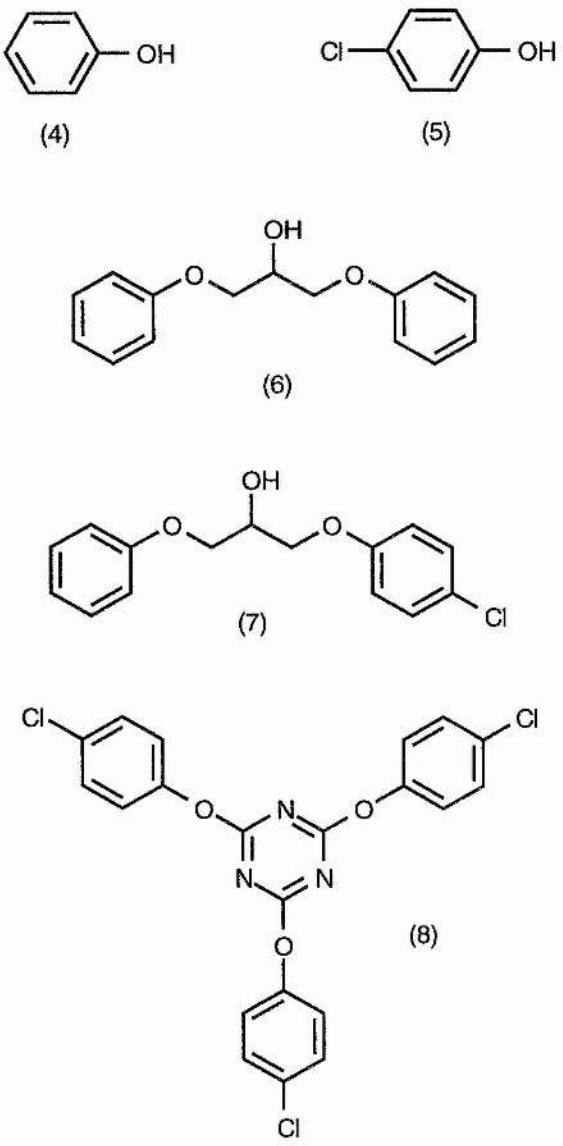
p-chlorophenyl cyanate

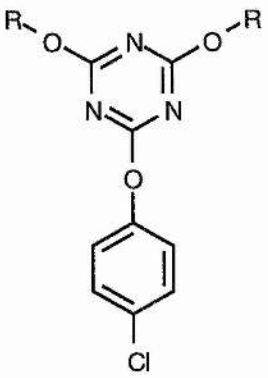
The main techniques for analysing product mixtures were high performance liquid chromatography (HPLC) and infra-red spectroscopy. One of the main conclusions, and the only definitive one made, is that reaction of *p*-chlorophenyl cyanate with phenyl glycidyl ether gives the same product mixture as the reaction of the *p*-chlorophenyl cyanate trimerisation product (tris-*p*-chlorophenyl cyanurate) with phenyl glycidyl ether, leading to the conclusion that the first step is the trimerisation of the cyanate ester.

The products of the reaction were separated through preparative HPLC and characterised where possible by comparison with reference compounds, although no details are given. Where no reference compounds were available for the more complicated products, infra-red, ^{13}C n.m.r. and mass spectra were used, but again very few details are given (only one ^{13}C n.m.r. spectrum is shown and even this has

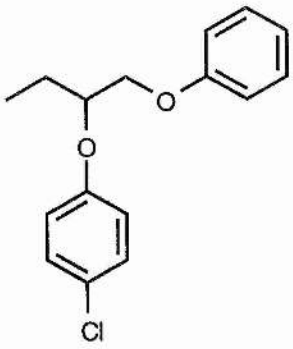
no chemical shift scale). The compounds allegedly identified were as follows (Fig. 3.7) with unreacted starting materials also being observed.

Fig. 3.7



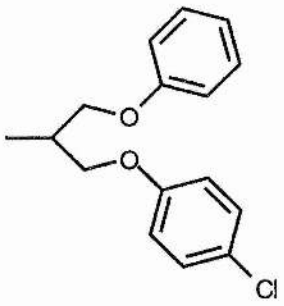


(9a) R =

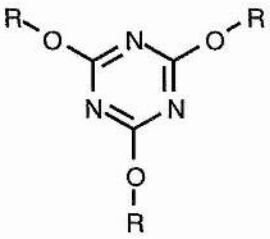


or

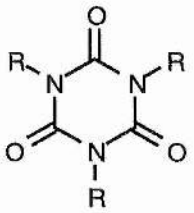
(9b) R =



depending on which carbon of the epoxy group is attacked

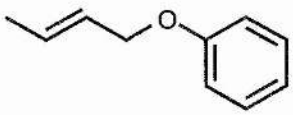


(10a), (10b) : R groups as above



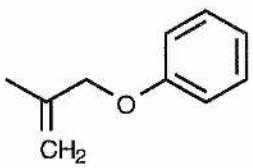
(11a), (11b) : R groups as above or

(11c) R =

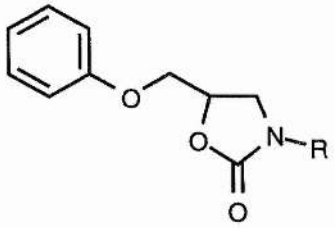


or

(11d) R =



resulting from the elimination of *p*-chlorophenol from the first two possibilities for R

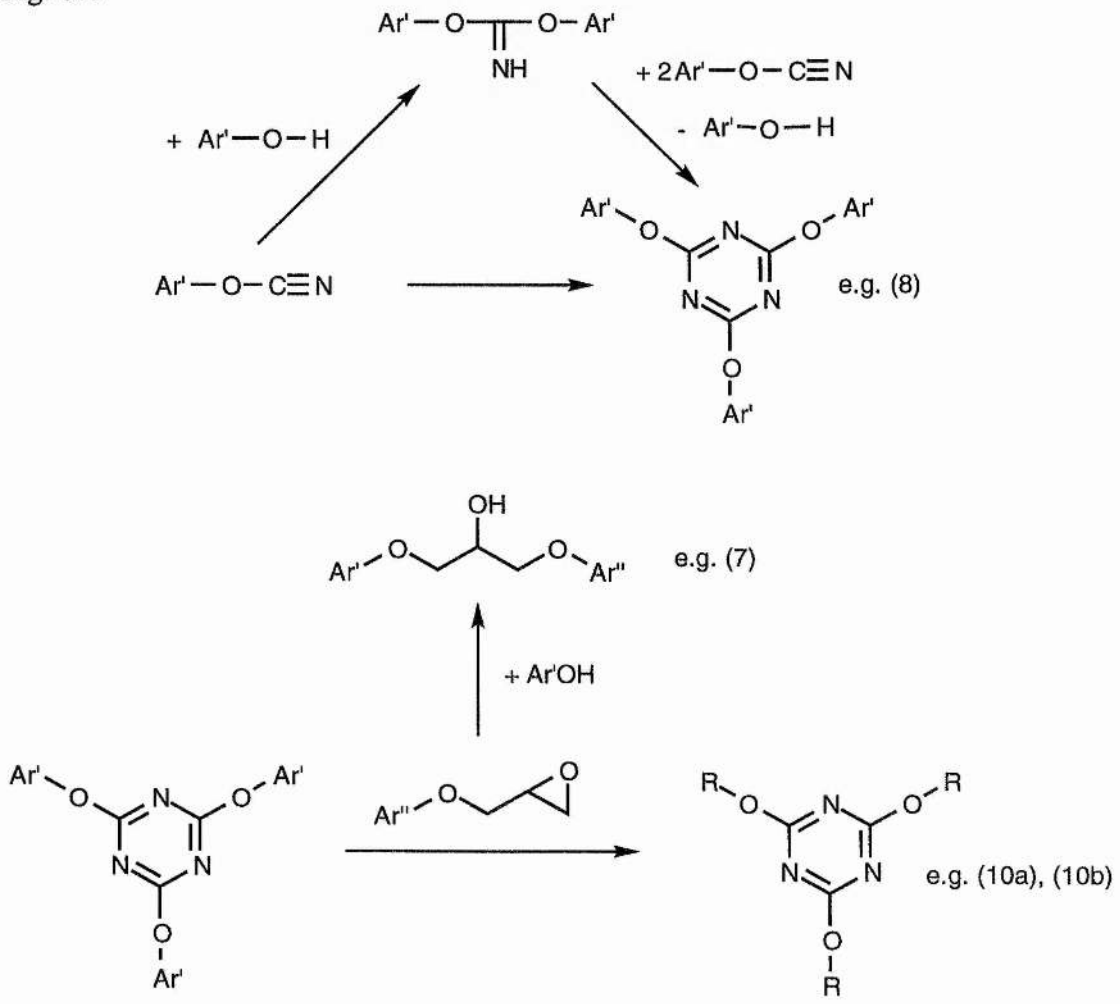


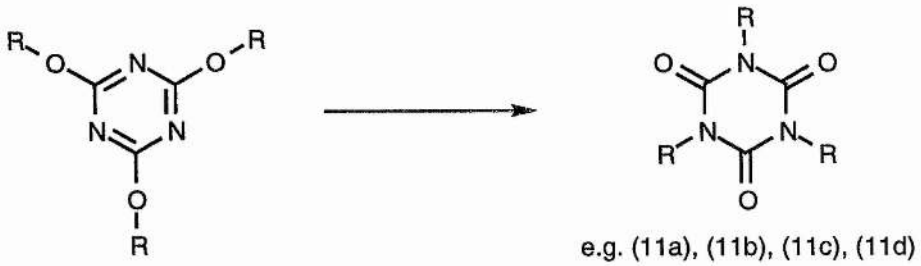
(12a), (12b), (12c) and (12d) :

R groups as above

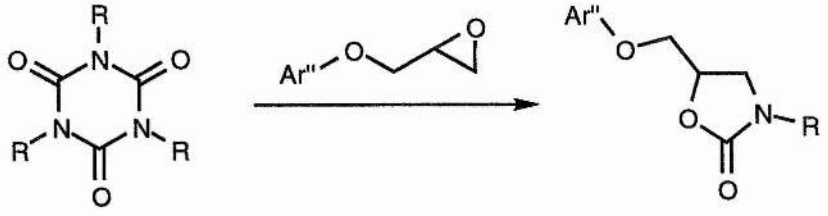
The evidence given for these compounds is not irrefutable (for instance there are more possible structures proposed than show up in the HPLC trace) but a succeeding paper[11] attempts to clarify the reaction pathways in a more systematic way. This results in the following reaction scheme (Fig. 3.8).

Fig. 3.8





e.g. (11a), (11b), (11c), (11d)



e.g. (12a), (12b), (12c), (12d)

Some inconsistencies are apparent between the products identified and the proposed reaction scheme. Firstly, phenol is a product but is not accounted for by the reaction scheme, in which it is alleged that only *p*-chlorophenol is eliminated from the more complicated structures "because it is more acidic than phenol"; however an elimination of phenol would also be expected to a degree. An alternative explanation for phenol production is outlined in Fig. 3.9 (below). Secondly, the epoxy insertion of the second step does not appear to be mechanistically sound. Thirdly, the scheme proposes the elimination of *p*-chlorophenol from each of the compounds after the epoxy insertion stage but no unsaturated alkyl cyanurates are observed as products. Fourthly, it is equimolar mixtures of cyanate ester and epoxide that are reacted but the oxazolidinone end-product is formed from one cyanate ester and two epoxide components.

Fig. 3.9

Whether or not this reaction pathway does indeed illustrate how cyanate esters and epoxides react cannot be stated unequivocally from this evidence, but what can be said is that if an oxazolidinone is the product of a co-reaction it is only one small component of a very complicated mixture of products (as illustrated by the HPLC data). Therefore the properties of any polymer formed in this way would be difficult to assign to specific structural components introduced. It also should be borne in mind that any co-reaction is also competing against homopolymerisation reactions of the cyanate ester and epoxide.

Having observed the work of the Bauer group[10,11], in 1992 Shimp presented more work[15] in this area examining the proposed reaction pathway described earlier. (Again the Martin reference is quoted as the original reference.) The Bauer pathway (Fig. 3.8) is presented although with an extra step added from the original claiming the 1:1 direct reaction of epoxide and cyanate ester to give the same oxazolidinone without the cyanurate and isocyanurate intermediates (even though the oxazolidinone product requires a 2:1 epoxide to cyanate ester stoichiometry). Also, in Shimp's first paper[14] he is talking about an oxazoline being formed, now it is an oxazolidinone but with oxazoline absorption bands being used for infra-red characterisation.

This paper uses *p*-cumylphenyl cyanate and phenyl glycidyl ether. The product mixtures were examined by gel permeation chromatography (GPC) and infra-red spectroscopy. However, the GPC results are perhaps given more significance than is appropriate.

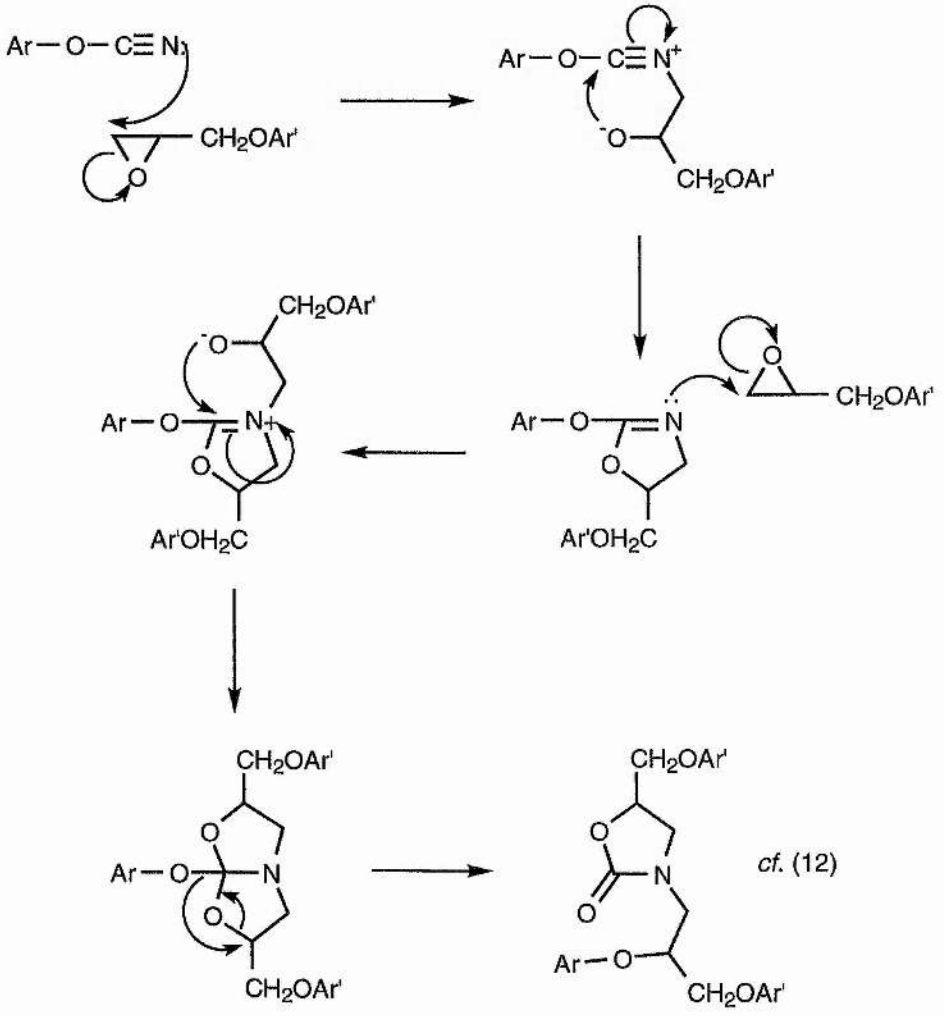
Gel permeation chromatography is generally used to show the molecular weight of a polymer, and to compare molecular weight distributions of a series of polymers of the same overall composition. Here it is being applied to give molecular weights of comparatively very small molecules without consideration for different shapes and polarities, a point highlighted by the fact that the molecular weights given for compounds for which a model was available are quite consistent across all the GPC traces, whereas the peak attributed to the oxazolidinone has an apparent molecular weight of 313 in one GPC trace (26% reacted) and molecular weight of 462 in another

(96% reacted)! Further evidence is clearly necessary to prove that these peaks actually correspond to the oxazolidinone.

Liquid chromatography results in the same paper are equally inconclusive: it is stated that 33 fractions were isolated, many of these being mixtures. Therefore it is conceivable that some of the GPC peaks are those of mixtures as well.

According to the reaction scheme the epoxy insertion products are formed and then converted into the oxazolidinone, but the GPC results suggest that the oxazolidinone is formed first. Again there is the problem of stoichiometry (2:1 epoxide to cyanate ester in the scheme; 1:1 in the reactions).

Fig. 3.10



There are so many inconsistencies in all these publications that it is difficult to accept their conclusions at face value in terms of the evidence presented. Further study of the subject was clearly warranted.

Other researchers have had the same thought and in 1994, when this project was already well under way, Fyfe *et al.*[16] published work attempting to provide further proof of oxazolidinone formation by techniques other than infra-red spectroscopy. He carried out this work believing that the literature from Bauer[10,11], Shimp[14,15], Gotro[40] and Martin[25] did not clearly establish the reactions involved. Thorough n.m.r. and mass spectroscopy characterisation was used to show that the main co-reaction product of epoxide and cyanate ester was indeed the oxazolidinone proposed by Bauer[11] and Shimp[15], but formed through a very different mechanism (Fig. 3.10) involving a 1,3-migration of an aryloxy group. The intermediates were not isolated.

Other co-reaction products identified were rationalised as arising from the carbamate formed from reaction of the cyanate ester with water (Fig. 3.11).

The presence of these compounds in the product mixture would also go a long way to accounting for the infra-red bands observed by the previous workers. However, it should be noted that the total amount of all co-reactions is only 12% of the overall reaction, the rest being the two self-reactions of the epoxide and the cyanate ester.

Further work in this area is still being published, the latest being by Grenier-Loustalot *et al* .[41] in 1995. Once more the work is based on that of Bauer[10,11], Shimp[14,15], Gotro[40] (and Martin[25]!), and, in the light of their low degree of concordance, attempts to clarify the situation. One thing that is clarified is the formation of the oxazolidinone by n.m.r.; however, they also put forward a new structure for the other major isolated co-reaction product, the result of the reaction between the carbamate (from cyanate ester and water) and the epoxide (Fig. 3.12).

Fig. 3.11

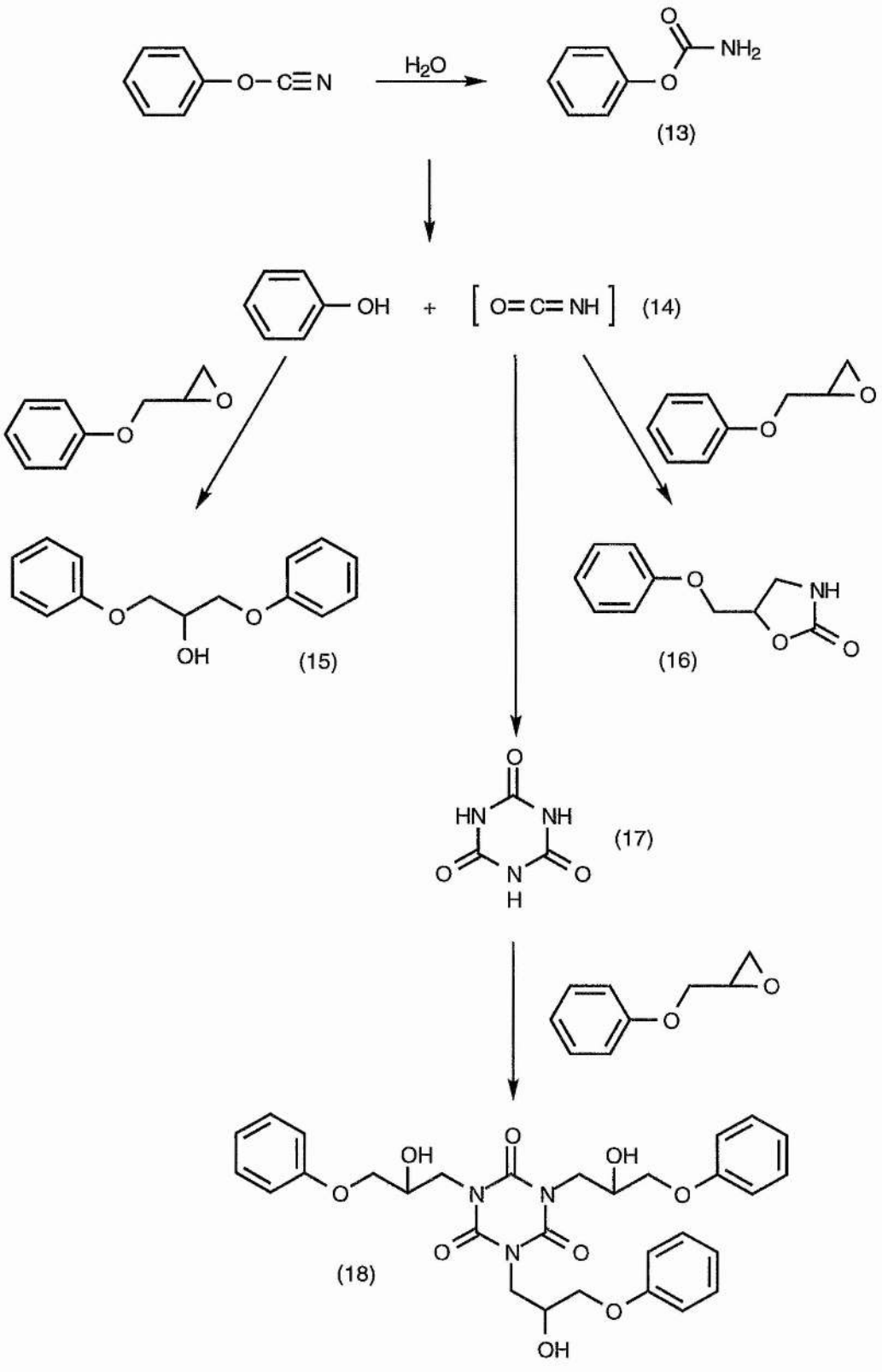
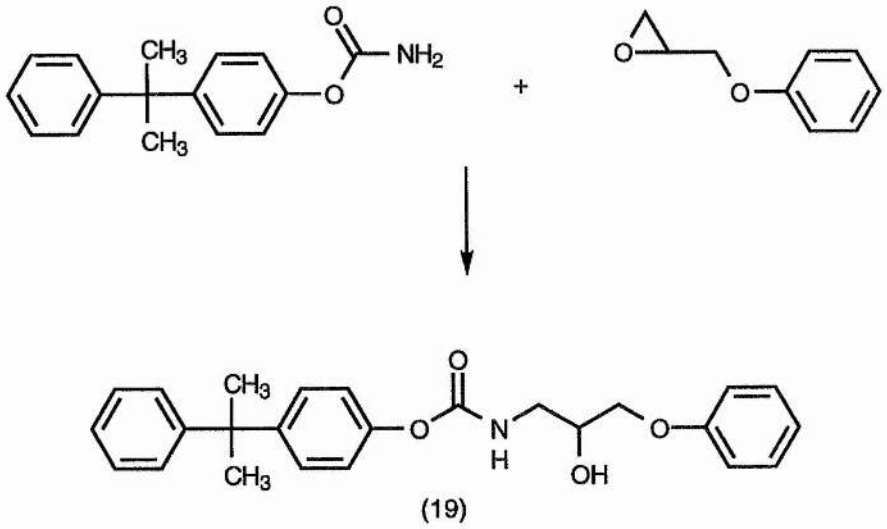


Fig. 3.12



(19)

Further epoxide polymerisation is then possible by ring-opening using the alcohol group (and possibly even the urethane amine group).

From the results of all the research groups there is little that can be conclusively stated about the cyanate ester and epoxide co-reaction. What all the papers agree upon is that undoubtedly there is a reaction occurring, but it is a very complicated system with many competing reactions taking place, of which only a small percentage are direct co-reactions. The work done in this chapter is intended, not to solve the mechanistic arguments over what is taking place, but to investigate the usefulness of the co-reaction as a predictable way of achieving the main aim of the project, i.e. finding a polymer system combining the better features of cyanate ester resins with the lower curing capabilities of epoxy resins.

3.2 Results & Discussion

A series of test reactions was carried out on monofunctional model compounds, namely *p*-chlorophenyl cyanate and phenyl glycidyl ether. Following the recommendations of Shimp *et al.*[15], some of the reactions were carried out in presence of copper(II) acetylacetonate and/or nonylphenol. The following conclusions were drawn.

p-Chlorophenyl cyanate trimerises at 150°C, with or without the presence of catalysts, giving 2,4,6-tris-(*p*-chlorophenyl) cyanurate (8).

Each of the catalysts individually accelerates the conversion of the cyanate ester into its trimer.

Phenyl glycidyl ether is unreactive at 150°C, whether or not a catalyst is present.

The 2,4,6-tris-(*p*-chlorophenyl) cyanurate does not react further in the presence of the catalysts at 150°C.

In a larger-scale reaction involving both the cyanate ester and the epoxide with the catalysts present, all the cyanate ester was used up, as was some of the epoxide. The product mixture was very complicated, as revealed by nine spots on a thin-layer chromatogram, and the mixture was separated as far as possible by column chromatography: 12 fractions were collected, each containing between one and four components (by t.l.c.). The cyanurate formed by the trimerisation of the cyanate ester was the major product, and *p*-chlorophenol was also shown to be present. All of the chromatographic fractions were examined by I.R. Carbonyl absorptions were found only in very minor fractions, and so it can be concluded that neither an oxazolidinone, e.g. (12) or (16), nor an isocyanurate, e.g. (11), (17), or (18), is formed in significant amount, if at all.

The major fractions were also examined by GC/MS. Four fractions studied in this way were as follows:

(i) This was insoluble in the chromatographic solvent (80:20 dichloromethane: petroleum) and had m.p. *ca.* 205°C. Its I.R. spectrum was similar (but not identical) to that of the cyanurate. The ion of highest *m/z* value in its mass spectrum was 400, and this did not obviously contain chlorine; the high-resolution mass measurement (Found: *m/z* 400.1207) corresponds most closely to $C_{27}H_{16}N_2O_2$ (400.1212) and $C_{25}H_{14}N_5O$ (400.1198), neither of which makes any sense in terms of the known starting compounds or the expected products. Fragment ions at *m/z* 375 and 358 suggest that the true molecular weight is higher than 400, and a series of ions at *m/z* 41 and 43, 55 and 57, 69 and 71, 83 and 85, 97, 111, 125, etc. suggest that the nonylphenol may even be involved. However the ^{13}C n.m.r. spectrum shows no trace of non-aromatic carbon. The nature of this compound or mixture is therefore still unknown.

(ii) The main component of this fraction was the tris(*p*-chlorophenyl) cyanurate, identified by comparison (t.l.c., I.R.) with an authentic sample.

(iii) The main component was identified as unreacted phenyl glycidyl ether.

(iv) The main component has a mass spectrum which is consistent with structure (7) (page 47): although no molecular ion is seen, fragment ions at *m/z* 167/169, 133 and 107 correspond to $ClC_6H_4OCH{=}CH\text{-}CH_2^+$, $C_6H_5OCH{=}CH\text{-}CH_2^+$ and $C_6H_5OCH_2^+$ respectively.

A further reaction involving a 1:3 ratio of tris(*p*-chlorophenyl) cyanurate (the triazine) to epoxide under the same catalysis at 150°C results in the same mixture of products (by I.R.) as the reaction involving equimolar proportions of the cyanate ester and the epoxide under the same conditions. This suggests that in the cyanate ester / epoxide reaction, the first step is the trimerisation of the cyanate, a conclusion which is in accord with the claims of Bauer[9-13] and Shimp[14,15].

These results do nothing to clear up the confusion already existing in the area of possible cyanate ester / epoxide co-reactions. Indeed they may serve only to increase the confusion. However they confirm that the first step is the trimerisation of the

cyanate ester, and also that any co-reaction is a minor reaction pathway by comparison with the self-reactions of the two individual reactants.

It was therefore decided that further pursuit of this strategy was likely to prove unprofitable in the short term, as far as the aims of this project were concerned. Attention was directed instead to a more predictable method for combining the cyanate/cyanurate functionality with that of an epoxide. Since the formation of the cyanurate was clearly the first step, the use of a cyanurate-based monomer became an attractive proposition. This forms the main part of Chapter 4.

3.3 Experimental

In these experiments the following abbreviations are used:

PGE = Phenyl glycidyl ether (1.3 mmol, 200 mg).

PCPcy = *p*-Chlorophenyl cyanate (1.3 mmol, 195 mg).

Trimer = Tris-(*p*-chlorophenyl) cyanurate (0.43 mmol, 198 mg).

NP = Nonylphenol (technical grade, 2% by weight).

Cu = Copper(II) acetylacetonate (250 ppm).

(The amounts of catalysts are based on Shimp's recommendations[15])

The reactions were carried out by stirring the reactants in an oil bath.

Reaction of the cyanate ester was indicated by the disappearance of the characteristic C≡N absorption band at 2250 cm^{-1}.

Reaction of the epoxide was indicated by the disappearance of the characteristic band at 910 cm^{-1}.

Test reactions

1) PGE + PCPcy + NP + Cu at 70°C for 5.5 h.

No reaction.

2) PGE + PCPcy + NP + Cu at 150°C for 5.5 h.

All cyanate ester and some epoxide used up.

3) Trimer + PGE + NP + Cu at 150°C for 5.5 h.

Identical (by I.R.) to the product of reaction 2).

4) PGE alone at 150°C for 5.5 h.

No reaction.

5) PCPcy alone at 150°C for 5.5 h.

Trimer produced (comparison with authentic sample).

6) PGE + NP + Cu at 150°C for 5.5 h.

No reaction.

7) PCPcy + NP + Cu at 150°C.

Mixture solidifies immediately. Trimer produced. (The catalyst merely speeds up the conversion).

8) PGE + PCPcy + NP at 150°C for 5.5 h.

All cyanate ester and some epoxide used up.

9) PGE + PCPcy + Cu at 150°C for 5.5 h.

All cyanate ester and some epoxide used up.

10) Trimer + NP + Cu at 150°C for 5.5 h.

No reaction.

Scale up of test reaction 2)

A mixture of phenyl glycidyl ether (9.2 g, 0.06 mol), *p*-chlorophenyl cyanate (9.5 g, 0.06 mol), nonylphenol (0.37 g) and copper(II) acetylacetonate (10 mg) was stirred at 150°C in an oil bath for 6.5 h. Once the mixture had cooled, diethyl ether was added and the insoluble product filtered off. The filtrate was concentrated, redissolved in 30:70 dichloromethane : petroleum, and chromatographed on silica gel. 50 fractions of 15 cm^3 were collected, the solvent mixture was then adjusted to 50:50, and a further 70 fractions each of 35 cm^3 were collected. At a solvent composition of 80:20, 280 fractions, and in pure dichloromethane 170 fractions, all of 35 cm^3, were obtained. Fractions were combined according to their compositions by t.l.c., even although few contained a single component. The solvents were evaporated off under reduced pressure; all residues were examined by I.R., and the four largest fractions by GC/MS.

The insoluble fraction (which was also insoluble in the chromatographic solvent mixture) is described on p. 57 under (i).

The three other major fractions, described on p. 57 as (ii), (iii) and (iv),were all eluted using the 30:70 and 50:50 solvent mixtures.

Tris-(*p*-chlorophenyl) cyanurate was prepared as described on p. 31.

1,3,5-Tris-(*p*-chlorophenyl)-1,3,5-triazine-2,4,6-trione [tris-(*p*-chlorophenyl) isocyanurate]

p-Chlorophenyl isocyanate (7.68 g, 0.05 mol) and potassium acetate (0.98 g, 0.01 mol) were heated together at 100°C. The mixture solidified almost immediately, but heating was continued for 3 h. The mixture was cooled, and the product recrystallised from dioxan or (better) tetrahydrofuran. Its m.p. (with decomposition) varied according to the rate of heating: 238-240°C in an open capillary, 250°C in a sealed tube, and 260°C in a sealed tube and a preheated block (lit.[42] 270°C). It shows the correct molecular ion at *m/z* 459 and has I.R. absorption (C=O) at 1700 cm^{-1}.

CHAPTER 4

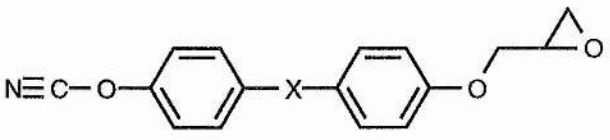
SOME EPOXY FUNCTIONALISED CYANURATES AND THEIR POLYMERISATION

4.1 Introduction

4.1.1 Monomer synthesis

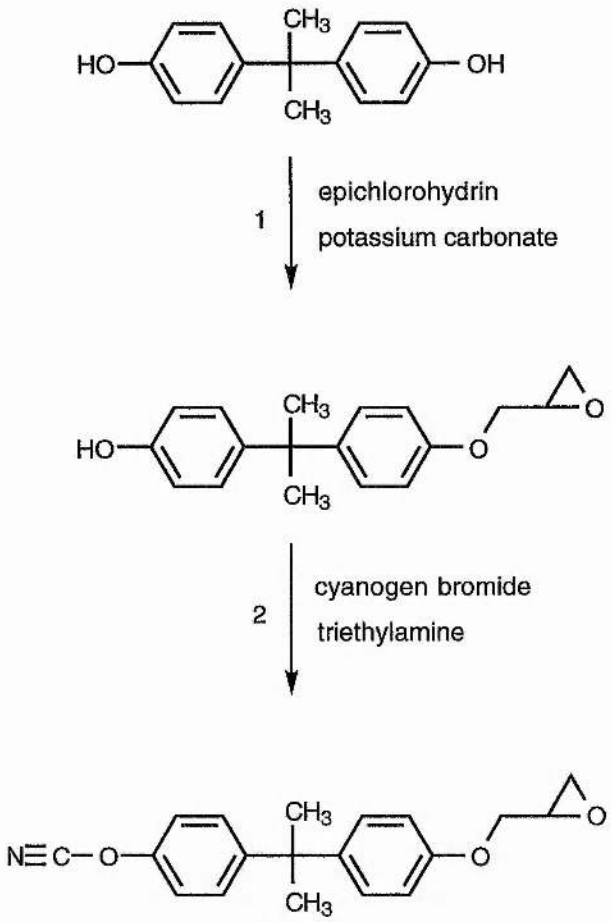
It has been described already (Chapter 1) how the main aim of this research is to find a way to marry the desirable properties of a cyanate ester resin with the lower curing capabilities of an epoxy resin. Plainly, mixing the two monomers and endeavouring to react them together is not an ideal solution (as shown in Chapter 3). It would be preferable to have a system where the curing reaction was more predictable and more easily controlled in order to attribute accurately any changes in polymer properties to changes in the integral structural components. The way to do this was deemed to require the synthesis of a monomer with both cyanate ester and epoxide functionalities. Polymerisation could then occur by homopolymerisation between monomers, cyanate ester with cyanate ester, epoxide with epoxide. Originally it was felt that a monomer such as that shown in Fig. 4.1 below would be needed. However it was felt that this compound would be subject to some synthetic difficulties due to the highly reactive nature of both functionalities. Also the stability might be low and storage-life not very long.

Fig. 4.1



Whilst this research was in progress, Fyfe *et al.*[17] published work on a mixed functionality monomer (cyanate ester and epoxide). Their idea was to use this compound to use the cyanate ester trimerisation as a means of crosslinking epoxy resins. The monomer was synthesised by the route shown below (Fig. 4.2).

Fig. 4.2



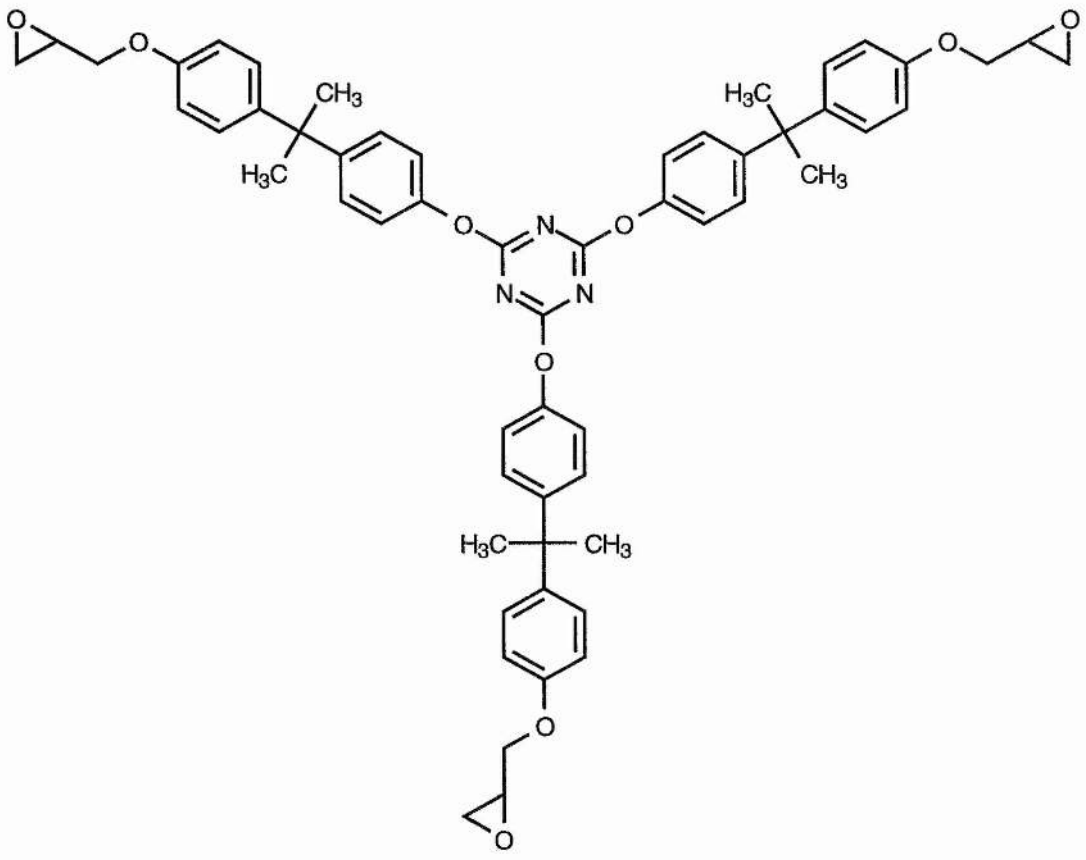
In step 1 the epichlorohydrin can react with either hydroxy group and (when using 1:1 stoichiometry of bisphenol A and epichlorohydrin) a mixture of unreacted bisphenol A, the desired bisphenol A monoglycidyl ether and unwanted bisphenol A diglycidyl ether is obtained. The bisphenol A monoglycidyl ether was purified by a complicated procedure involving extraction and column chromatography, and finally obtained in a yield of 18.9%. The second step is a straightforward cyanation of the type discussed in

Chapter 2, with a yield of bisphenol A monocyanate monoglycidyl ether of 88%. This means that the overall yield is 16.6%.

This monomer is used to crosslink cyanate esters and epoxides by heating it with a cyanate ester to incorporate it into the cured cyanate ester resin, at which point it can subsequently react with the epoxide under base catalysis. Alternatively it can be used by simultaneously curing all three components (epoxy monomer, cyanate ester monomer and bifunctional monomer) together in the presence of both base curing agent and heat. It is claimed that materials formed in this way are much tougher and stronger than those formed by previous co-reaction methods.

Fyfe's paper also touches on the concept upon which this chapter's work is based, namely that a triazine derived from a bifunctional monomer (Fyfe's monomer is shown

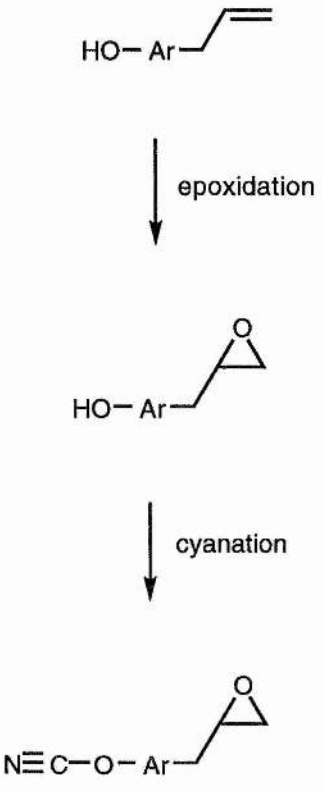
Fig. 4.3



in Fig. 4.3 above) could be used to crosslink epoxy resins alone, thus providing a cyanurate back-bone to an epoxy resin.

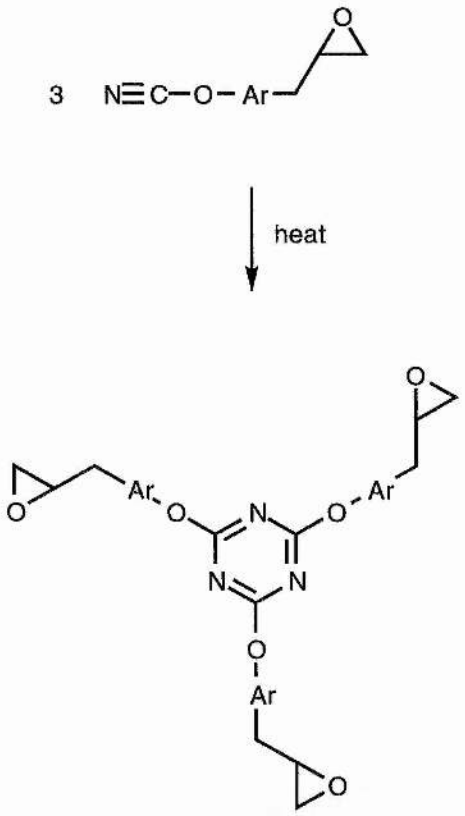
This is done by Fyfe *et al.* by trimerising a bifunctional epoxide / cyanate ester monomer. However, it would be an advantage to find a synthesis of such a bifunctional monomer which avoids the non-selective (and therefore low-yielding) epoxidation step in the synthesis. A possible method for this would be to start from an allyl phenol, epoxidise the double bond and cyanate the hydroxyl to give the required bifunctional monomer (as shown in Fig. 4.4). This monomer might then be trimerised by heating to give a tris(epoxy-functionalised) cyanurate (Fig. 4.5). This would be an epoxy monomer capable of introducing cyanurate character into an epoxy resin system only using epoxy polymerisation methods.

Fig. 4.4



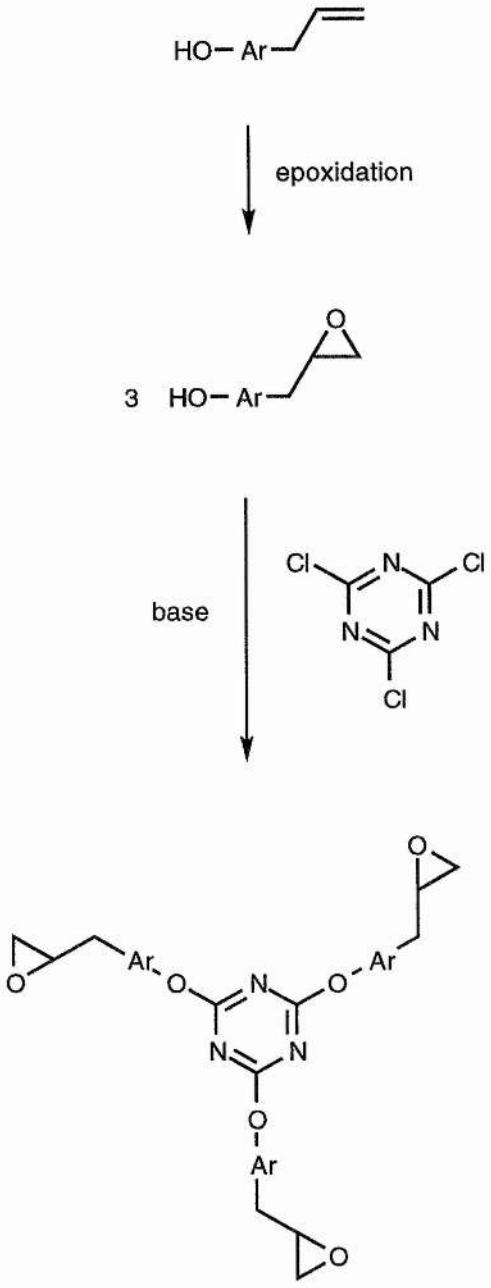
However, there are two disadvantages immediately apparent in this proposed scheme. The first is that the synthetic problems of producing a monomer with two very reactive groups are still present, and secondly that the trimerisation step still requires the higher temperatures which have already been identified (Chapter 1) as one of the main drawbacks of cyanate ester resins, and one of the reasons for the study of their combination with epoxy resins.

Fig. 4.5



An alternative reaction scheme could perhaps avoid both of these problems (Fig. 4.6). In this way the bifunctional, epoxide and cyanate ester containing, compound is avoided and the cyanurate structure is obtained, not by trimerisation of a cyanate ester by heating, but simply by reaction of the appropriate alcohol with cyanuric chloride (a cheap and readily available compound) under basic conditions.

Fig. 4.6



4.1.2 Polymer synthesis

Polymers need to be made with cyanurate monomers synthesised as above to investigate the properties. The alcohols chosen for these purposes were eugenol and glycidol, as described in the rest of this chapter. The most important information to be

gathered from these polymers is the observation of property trends which appear due to the variation of the amount of cyanurate monomer added to an epoxy polymer. In this way the effect of the incorporated cyanurate structure can be identified.

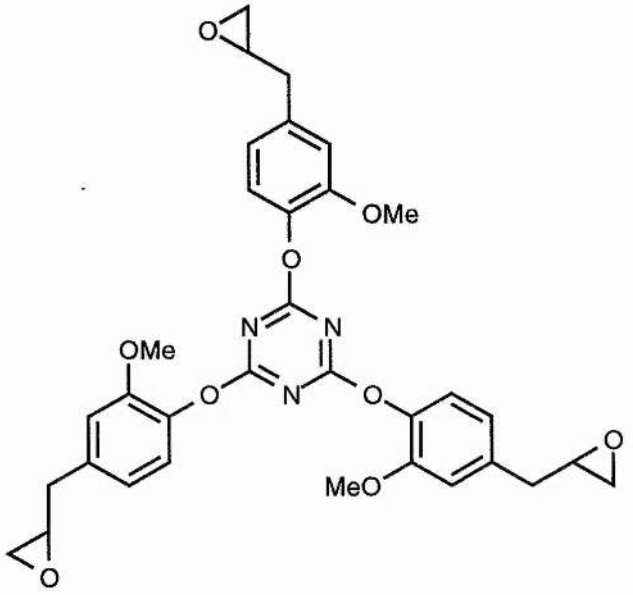
To do this a standard epoxy resin system is required to be doped with increasing amounts of a cyanurate monomer. The system chosen was based on Epon 828, a readily available and commercially popular epoxy monomer, with which the use of different amines and cure catalysts was possible. It is also necessary to prepare standard polymers under the same conditions as the novel polymers in order that fair comparisons can be made. These polymers then need to be tested for general properties as well as others specific to the particularly important applications. These include mechanical testing (modulus, stress, strain, T_g, fracture toughness), measurement of water absorption and of dielectric constant.

4.2 Results & Discussion

4.2.1 Monomers

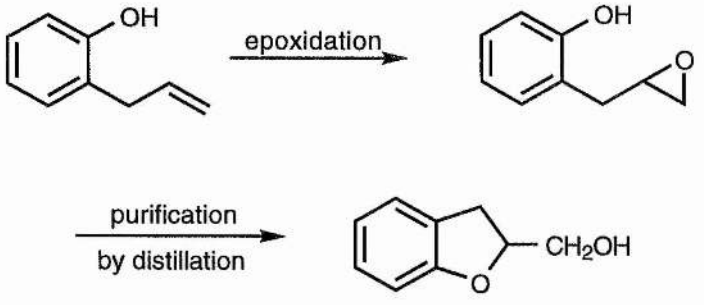
Epoxy eugenol was successfully synthesised and further reacted with cyanuric chloride to give trisepoxyeugenyl cyanurate (Fig. 4.7).

Fig. 4.7



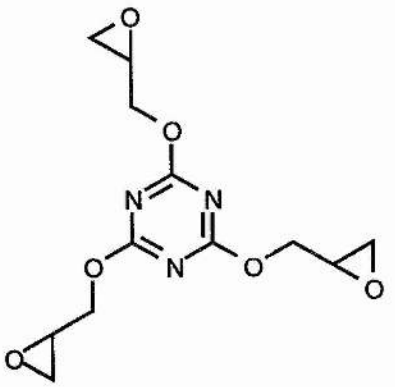
The synthesis of an analogue with the epoxy group *ortho* to the ether link is not possible by this method as the *ortho*-epoxy group reacts with the phenol readily to give a five membered ring[43] (Fig. 4.8).

Fig. 4.8



Triglycidyl cyanurate (Fig. 4.9) was also successfully synthesised, from glycidol and cyanuric chloride, to provide a second monomer for polymerisation studies.

Fig. 4.9



4.2.2 Polymers

It should noted that these experiments should be regarded as a series of preliminary or "scouting" experiments mainly concerned with the observation of trends.

4.2.2.1 Nomenclature

The precise composition of each polymer is described in the experimental section 4.3, but the general nomenclature used is as follows:-

POL. = polymer.

STA. = standard.

The non-standard polymers were all based on the Epon 828 epoxy resin and 4,4'-diaminodiphenyl sulfone (DDS) curing agent system (unless otherwise stated) with additional components as specified below.

TEEC. = containing trisepoxyeugenyl cyanurate.

TGC. = containing triglycidyl cyanurate.

The number following TEEC. or TGC. represents the percentage of that monomer in the epoxy component of the mixture, the remainder being Epon 828.

PACM= bis-*p*-aminocyclohexyl methane curing agent instead of DDS.

TET. = containing TILCOM TET catalyst .

TAA. = containing TILCOM TAA catalyst .

BF_3. = containing BF_3-monoethylamine catalyst .

4.2.2.2 General observations

All the standard polymers (POL.STA.1-6) were successfully prepared as described in section 4.3.2.

POL.TEEC/TGC.0.PACM could not be prepared free from bubbles because it polymerises before all the solvent has evaporated off.

The TEEC range of polymers (POL.TEEC/TGC.0, POL.TEEC.5, POL.TEEC.10, POL.TEEC.25 and POL.TEEC.50) was successfully prepared with a darkening in colour noticed as the concentration of TEEC increased. (All of these epoxy based polymers were transparent.)

In the TGC range of polymers (POL.TEEC/TGC.0, POL.TGC.5, POL.TGC.10 and POL.TGC.25) most were prepared successfully, a darkening in colour again being noticed as the amount of TGC was increased. However, for POL.TGC.50, numerous circular patterns were present in the resin. These were very thin circles of diameter between 1 mm and 10 mm of a "spoked" nature. This polymer was very brittle.

It was believed that these circles were stress fracture patterns caused by too high a cross-link density. The fact that this occurred with POL.TGC.50 and not POL.TEEC.50 suggests that the cross-link density is higher in POL.TGC.50. This is consistent with the fact that TGC is a significantly smaller molecule than TEEC and therefore the epoxy groups are closer together and the cross-link density would be greater. Another possible explanation is that for some reason POL.TGC.50 had cured to a greater degree than POL.TEEC.50.

TILCOM TET is a catalyst which allows a DDS / epoxy resin to cure at ~130°C (see experimental section, 4.3)[44]. It was used to prepare the next three polymers.

POL.TEEC/TGC.0.TET was prepared successfully. POL.TEEC.10.TET however turned out to be very brittle with some long cracks on the lower face. Then, somewhat

inconsistently, POL.TEEC.25.TET was prepared with no such problems. The only explanation for this anomaly was offered by the "blotchy" appearance of POL.TEEC.10.TET, where some TEEC had apparently crystallised out and coagulated together. This must have something to do with the brittleness, as analogues containing both less TEEC and more TEEC do not have such problems.

Another observation made was that these polymers are again progressively darker with more TEEC present, although no comparison can be made with the uncatalysed polymers' colours as the catalyst itself introduces colour to the polymer.

TILCOM TAA is another catalyst which allows a DDS / epoxy system to cure at a lower temperature, this time ~90°C[44] (see experimental section, 4.3). It was used to prepare the next three polymers.

POL.TEEC/TGC.0.TAA, like POL.TEEC/TGC.0.TET, was prepared successfully. POL.TEEC.10.TAA however suffered from a multitude of small, "crumbly" cracks on the lower surface. These are not readily explicable, although it is as if most of the catalyst had "sunk" to the bottom of the mixture and the mixture was overcured on the lower face of the polymer but not on the upper. This hypothesis is difficult to justify, however, when it is considered that this did not occur with POL.TEEC/TGC.0.TAA or indeed with POL.TEEC.25.TAA which, although did contain bubbles through curing before all the solvent could be removed, did not have lower surface cracks.

This fact that POL.TEEC.25.TAA cured prematurely but POL.TEEC.10.TAA and POL.TEEC/TGC.0.TAA did not suggests that the amount of TEEC present affects the progress of the curing reaction. This is possible due to the triazine nitrogen atoms which could act to open epoxide rings in the manner of a tertiary amine. However, repeat experiments, not possible due to limited amounts of monomers, would be necessary to prove that this was not an anomaly put down to slightly more solvent to evaporate off, a slightly higher oven temperature or other condition change.

BF_3-monoethylamine complex is commonly used in DDS / epoxy systems to ensure complete curing[44]. It was used in the preparation of the next three polymers.

POL.TEEC/TGC.0.BF_3 and POL.TEEC.10.BF_3 were prepared successfully but POL.TEEC.50.BF_3 had some fracture patterns in it. These patterns (unlike those in POL.TGC.50) were of an irregularly circular nature, "outline" circles rather than ones with internal structure, and relatively large (10 mm to 30 mm diameter). There was no such occurrence with POL.TEEC.50 (i.e. without the BF_3-monoethylamine complex) which again leads to the conclusion that the catalyst may lead to a greater extent of cross-linking and that POL.TEEC.50 may not be cured to so great an extent.

4.2.2.3 Mechanical testing

Flexural stress and strain testing can give lower results than are in fact true due to surface imperfections in the polymer samples used. These surface imperfections can provide points on the material from where cracks can propagate.

This is also the case to a greater extent for tensile stress and strain testing. This is because in flexural testing the maximum force is only applied along one line on the lower side of the sample, whereas in tensile testing it is applied evenly on all four sides, hence increasing the probability of coinciding with an imperfection.

4.2.2.3.1 Flexural strain

Flexural strain results were averaged from six experiments and the results are shown in Table 4.1 (below).

Table 4.1

Polymer	Flexural strain (%)	Standard deviation (%)
POL.STA.1	3.302	0.754
POL.STA.2	4.828	1.178
POL.STA.3	3.816	1.136
POL.STA.4	3.978	0.776

Table 4.1 (cont.)

Polymer	Flexural strain (%)	Standard deviation (%)
POL.STA.5	3.186	0.480
POL.STA.6	2.520	0.307
POL.TEEC/TGC.0	7.515	0.820
POL.TEEC.5	7.461	2.401
POL.TEEC.10	6.938	1.286
POL.TEEC.25	6.396	1.579
POL.TEEC.50	3.140	0.489
POL.TGC.5	7.932	1.420
POL.TGC.10	9.713	1.581
POL.TGC.25	7.425	1.793
POL.TEEC/TGC.O.TET	9.264	1.060
POL.TEEC/TGC.0.TAA	7.685	1.594
POL.TEEC.25.TET	3.900	0.382

Fig. 4.10 (below) compares the standard polymers together. POL.STA.2, the epoxy resin, allows the highest degree of bending with the cyanate ester resins having significantly lower values (the next closest being ~18% less). POL.STA.6, the "low-curing" cyanate ester, was very brittle, some of the pieces breaking the instant some force was applied.

Fig. 4.10

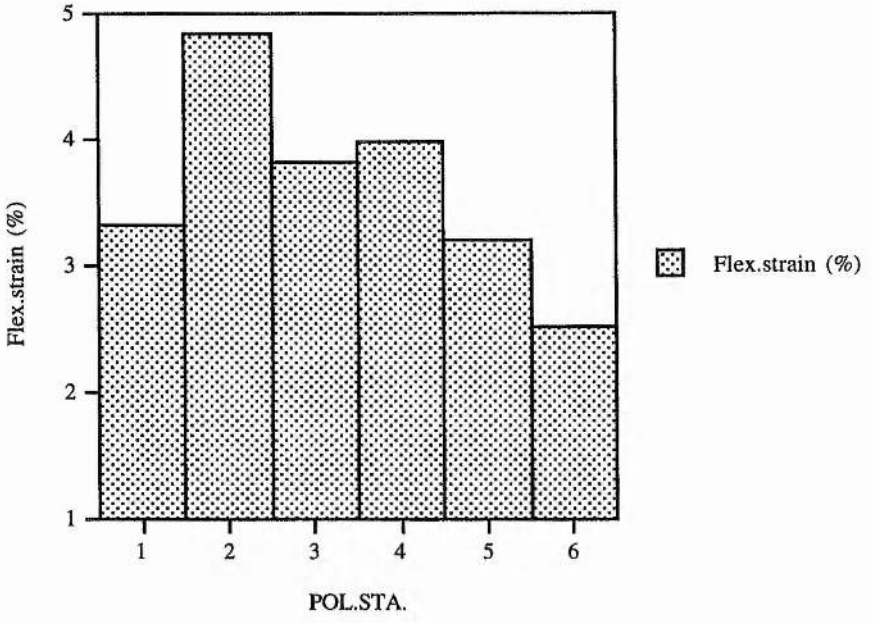


Fig. 4.11

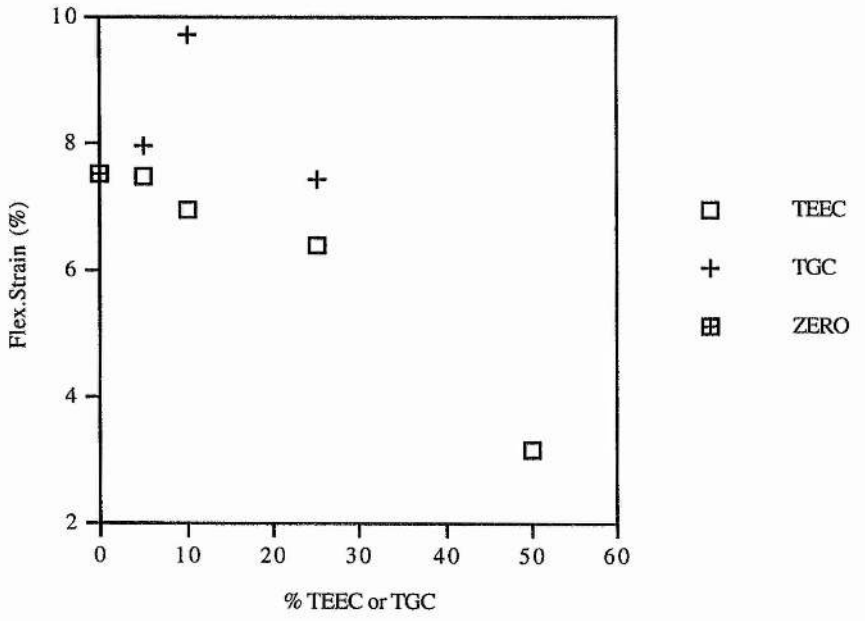
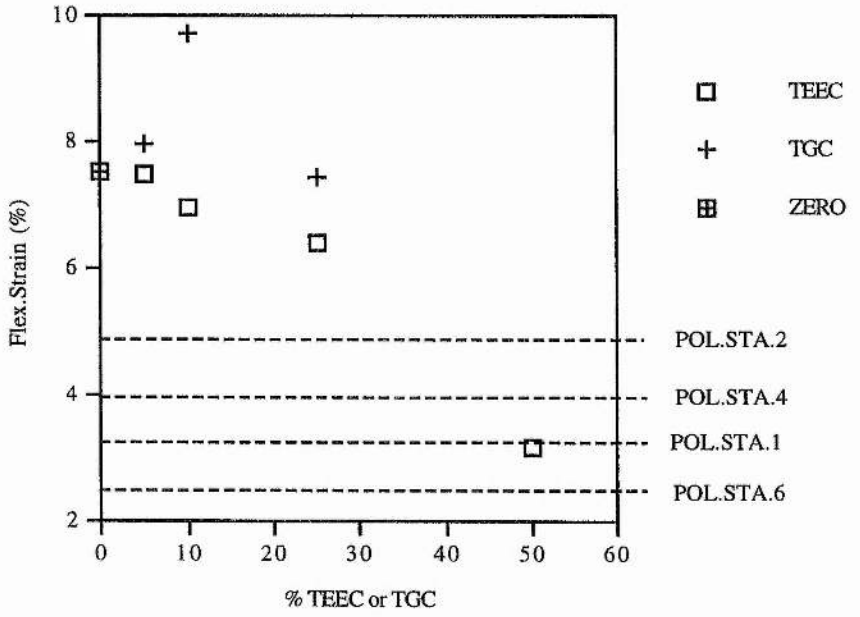


Fig. 4.11 (above) shows how adding TEEC or TGC to the Epon 828 / DDS epoxy system affects the flexural strain. In the case of TEEC there is a general trend for the flexural strain to decrease with an increase in the amount of TEEC present, i.e. the higher flexural strain characteristic of an epoxy resin decreases towards the lower values characteristic of a cyanate ester resin. This is consistent with the increasing in the amount of cyanurate structure bringing more cyanate ester resin character to the polymer.

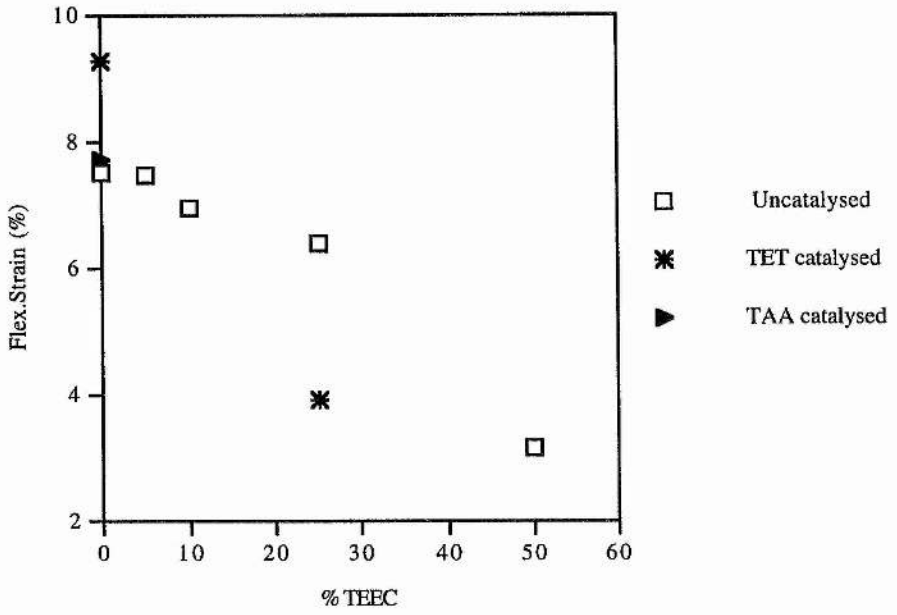
This trend, however, is not as clear in the case of TGC, a fact that is not readily explicable.

Fig. 4.12



If these results are then compared with some of the standard polymers (Fig. 4.12) where the dashed lines show the flexural strain values for the standards) it is seen that only the 50% TEEC polymer (POL.TEEC.50) has a flexural strain lower than most of the standards.

Fig. 4.13



There are also the catalysed analogues of POL.TEEC/TGC.0 and POL.TEEC.25 to compare (Fig. 4.13 above).

POL.TEEC/TGC.0.TAA has a similar flexural strain value to that of the uncatalysed, but cured at a higher temperature, analogue POL.TEEC/TGC.0, whereas POL.TEEC/TGC.0.TET has a higher value. With the knowledge that TILCOM TET is not as effective a curing catalyst as TILCOM TAA (see experimental section 4.3) this higher value could be explained by POL.TEEC/TGC.0.TET not being cured to the same extent as POL.TEEC/TGC.0.TAA. However, it does not explain the fact that POL.TEEC.25.TET has a lower flexural strain than POL.TEEC.25 when POL.TEEC.0.TET has a higher flexural strain than POL.TEEC.0. There may be a combined effect between the catalyst and the cyanurate nitrogen atoms, but it is of course important not to draw too many conclusions about a trend when only two points have been obtained.

4.2.2.3.2 Flexural stress

Table 4.2

Polymer	Flexural stress (N/mm^2)	Standard deviation (N/mm^2)
POL.STA.1	95.63	21.48
POL.STA.2	153.1	29.27
POL.STA.3	113.3	30.00
POL.STA.4	121.8	23.27
POL.STA.5	106.5	16.78
POL.STA.6	78.55	12.66
POL.TEEC/TGC.0	139.3	8.394
POL.TEEC.5	138.2	26.57
POL.TEEC.10	148.5	13.87
POL.TEEC.25	150.4	27.36
POL.TEEC.50	98.09	14.74
POL.TGC.5	149.9	14.51
POL.TGC.10	173.0	10.85
POL.TGC.25	164.9	21.51
POL.TEEC/TGC.O.TET	187.3	7.180
POL.TEEC/TGC.0.TAA	184.3	16.39
POL.TEEC.25.TET	120.5	26.71
POL.TEEC/TGC.0.BF_3	138	*
POL.TEEC.10.BF_3	153	*

* Tested by ICI staff with no standard deviation given.

Flexural stress results were averaged from six experiments: however they should not be taken as definitive values for flexural stress. The problem is that the expression used to calculate flexural stress ($3FS / 2BW^2$) (see experimental section 4.3) does not apply when $\delta >> W$ (i.e. the extent of bending is more than the sample's thickness), and with some of these samples this could be the case. The polymers with lower flexural strain are fine in this respect, so most of the standard polymer results are acceptable, but there may be some false values for some of the polymers with higher flexural strain. The results are tabulated above (Table 4.2).

Fig. 4.14

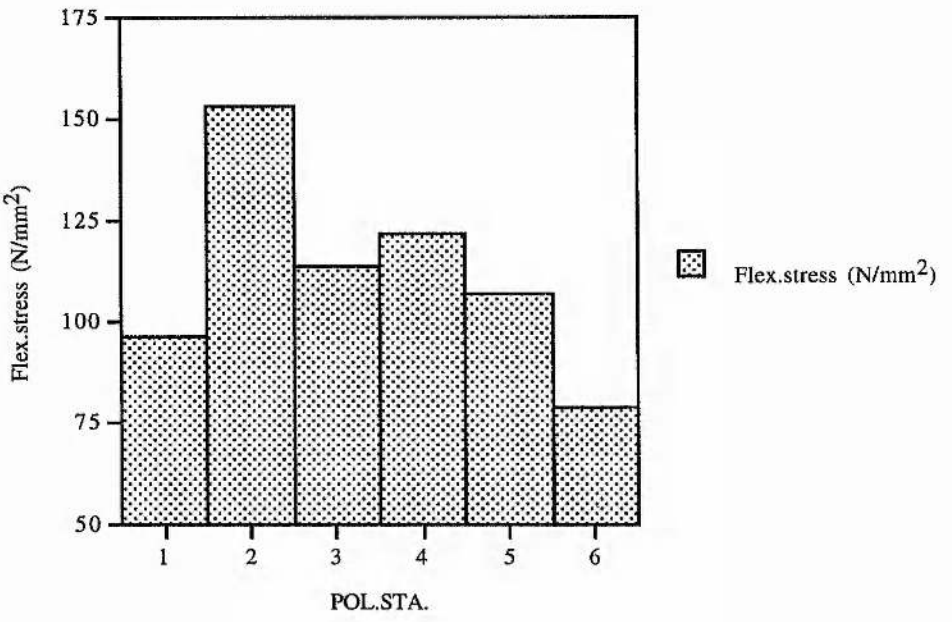


Fig. 4.14 (above) compares the standard polymers together. The pattern is very similar to that for flexural strain with the highest value belonging to the epoxy resin (POL.STA.2) and lowest to the very brittle "low-cured" cyanate ester resin (POL.STA.6). The epoxy resin has a significantly higher value for flexural stress than the cyanate ester resins, just as it has for flexural strain.

From these results it would be expected that with the TEEC- and TGC- containing polymers the flexural stress would decrease with the amount of either cyanurate monomer present in the monomer mixture. However, as can be seen from Fig. 4.15 (below) this does not appear to be the case except for POL.TEEC.50. There are not enough points on the graphs to prove this, but it appears that in both the TEEC and TGC systems there may be a peak value at ~18% cyanurate composition.

If these results are then compared with some of the standard polymers (Fig. 4.16) it can be seen that most of these polymers have flexural stress values comparable with the epoxy resin (POL.STA.2), and that only POL.TEEC.50 has a similar value to the cyanate ester resins. Again it should be emphasised that caution must be observed in the rigorous interpretation of the results due to the problem of the extent of bending making the calculation invalid.

Catalysed analogues can be compared with the TEEC range of polymers (Fig. 4.17 below).

Fig. 4.15

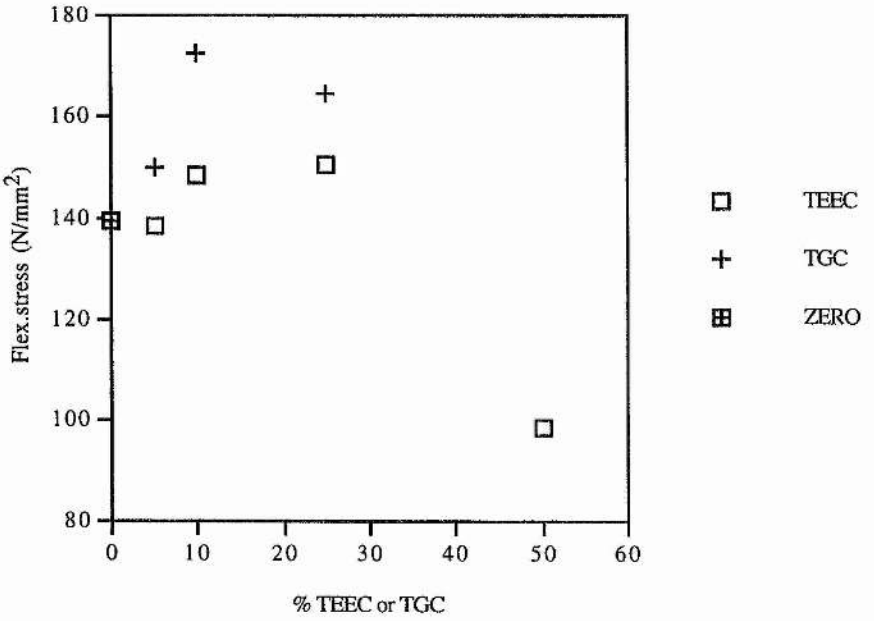


Fig. 4.16

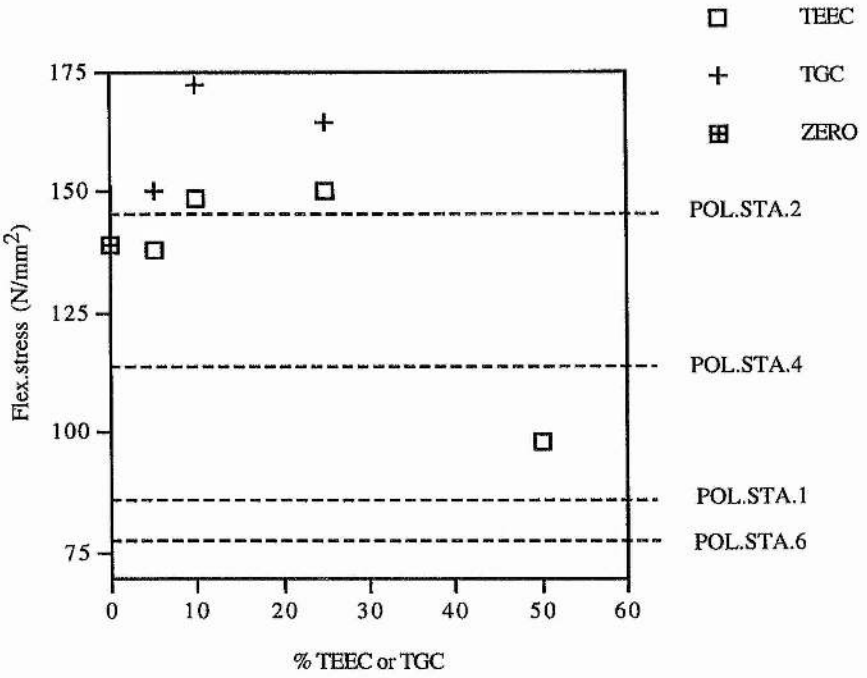
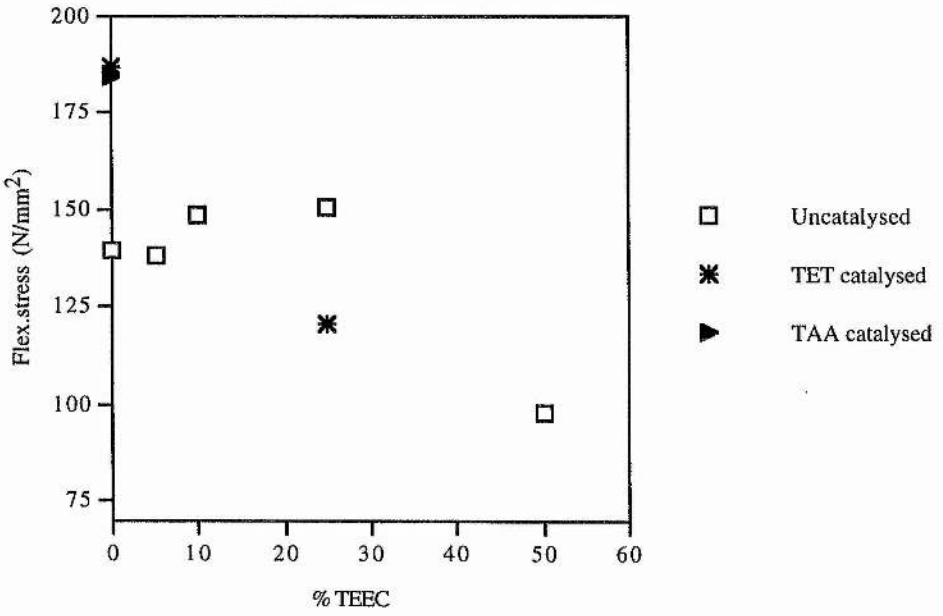


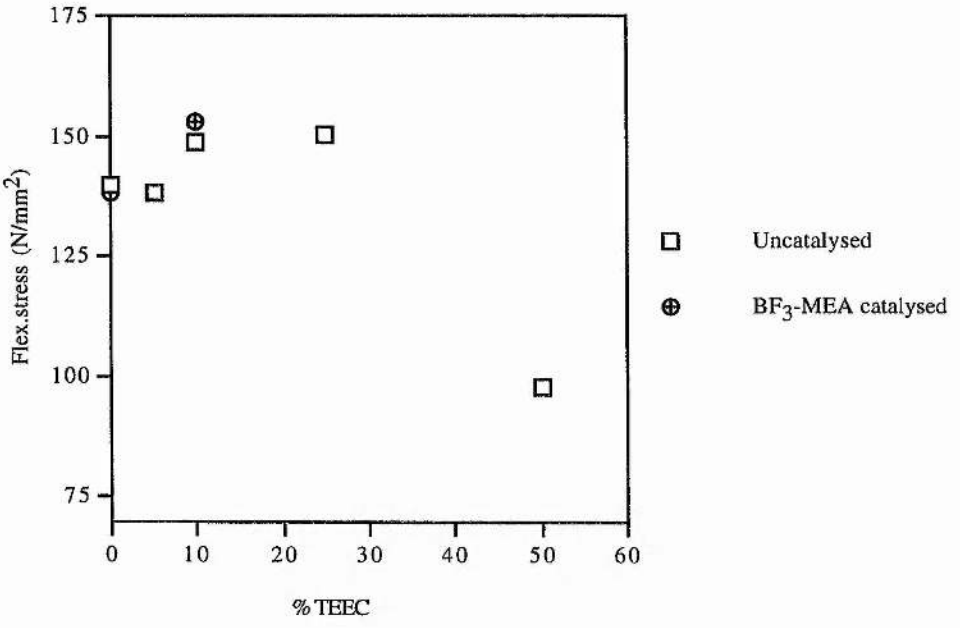
Fig. 4.17



On this occasion the flexural stress values for POL.TEEC/TGC.0.TET and POL.TEEC/TGC.0.TAA are very similar, but much higher than for the equivalent polymer without a catalyst (POL.TEEC/TGC.0). However, POL.TEEC.25.TET has a lower flexural stress than POL.TEEC.25, so it is difficult to see any pattern emerging. The degree of curing in each case may again be important, as may be flexural stress calculation restrictions.

Two other polymers were measured for flexural stress: POL.TEEC/TGC.0.BF_3 and POL.TEEC.10.BF_3. These are analogues of POL.TEEC/TGC.0 and POL.TEEC.0, both cured with BF_3-monoethylamine complex also present to ensure complete curing, and both are compared in Fig. 4.18 (below).

Fig. 4.18



It can be seen that the polymers cured with BF_3-monoethylamine complex give very similar results to the two polymers of the same composition without BF_3-monoethylamine present. Therefore, if it is assumed that the calculation for flexural stress is applicable for these polymers, either the degree of curing is the same with or

without BF_3-monoethylamine complex present or the degree of curing does not have any marked effect on this property of the resins.

4.2.2.3.3 Modulus by flexure

Table 4.3

Polymer	Modulus by flexure (N/mm^2)	Standard deviation (N/mm^2)
POL.STA.1	2824	161
POL.STA.2	3579	130
POL.STA.3	3147	87
POL.STA.4	2978	181
POL.STA.5	3354	35
POL.STA.6	3409	21
POL.TEEC/TGC.0	2391	56
POL.TEEC.5	2473	26
POL.TEEC.10	2759	30
POL.TEEC.25	2918	27
POL.TEEC.50	3484	74
POL.TGC.5	2587	42
POL.TGC.10	2661	99
POL.TGC.25	3059	42
POL.TEEC/TGC.O.TET	2636	43
POL.TEEC/TGC.0.TAA	3132	65
POL.TEEC.25.TET	3414	44
POL.TEEC/TGC.0.BF_3	3000	*
POL.TEEC.10.BF_3	3400	*

* Tested by ICI staff with no standard deviation given.

Modulus measured by flexure was calculated by averaging results from six samples. It has been pointed out by Dr. R. Moore of ICI that, due to the relative length and thickness of the samples tested, there is also a shear contribution to the modulus of ~3%, meaning that the results quoted below (Table 4.3) are ~3% below the correct values. However, with all the samples being of similar size and the main discussion being centred around comparisons between the moduli of these polymers, it was deemed unnecessary to take this shear contribution into account at the present stage.

Fig. 4.19

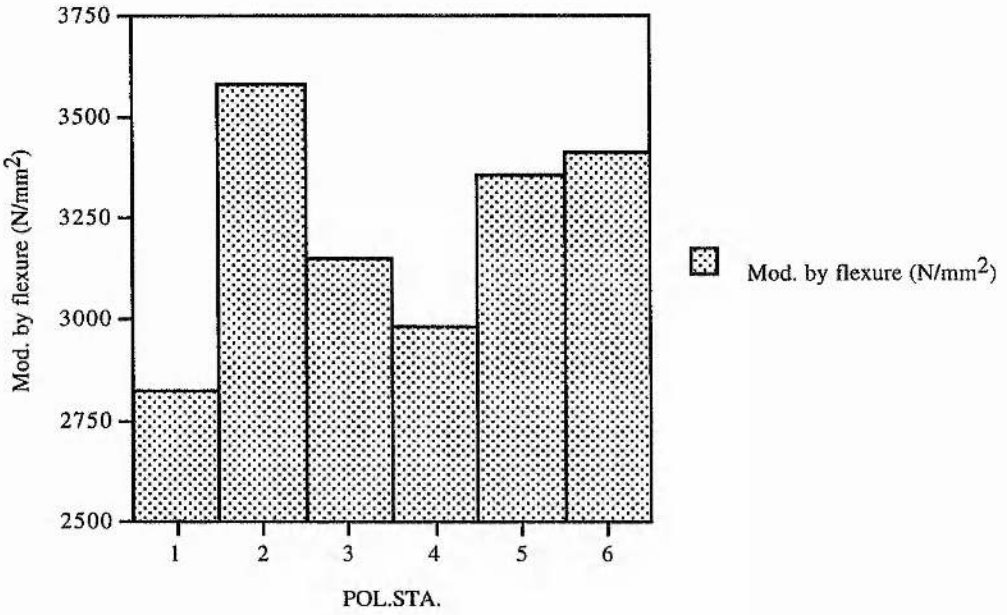
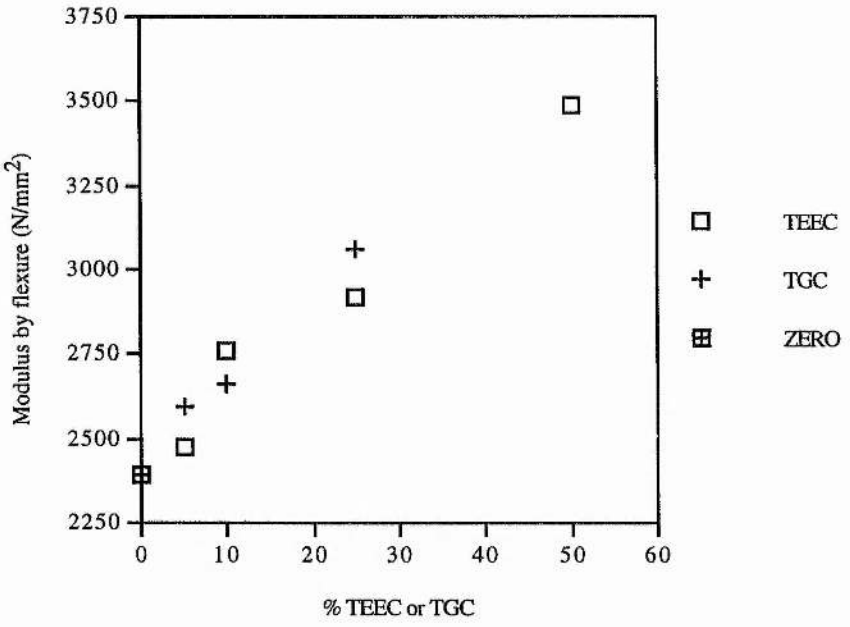


Fig. 4.19 (above) compares the moduli measured by flexure of the standard polymers. The epoxy resin (POL.STA.2) has the highest modulus, followed by the low temperature cured cyanate ester (POL.STA.6).

From this it may be expected that the modulus would decrease on increasing the amount of TEEC or TGC included in the Epon 828 / DDS system. However, 934 epoxy (POL.STA.2) is a toughened epoxy resin which contains hardening agents, and in fact Epon 828 cured with DDS (POL.TEEC/TGC.0) has a lower modulus than all

the standard cyanate ester resins. Furthermore, increasing the amount of cyanurate monomer (TEEC or TGC) in the Epon 828 / DDS system leads to an *increase* in modulus as can be seen in Fig. 4.20 (below), i.e. the more cyanurate structure included the stiffer the polymer becomes.

Fig. 4.20



Unlike flexural stress and flexural strain, in the case of modulus measured by flexure very similar results are obtained, irrespective of whether the cyanurate containing monomer used is TEEC or TGC. Therefore the most important factor in increasing the modulus by increasing the amount of cyanurate included in the polymer appears to be the overall proportion of cyanurate rings, not how close together the individual triazine rings are located in the polymer structure.

When these results are compared with the standards (Fig. 4.21 below) it is seen that a proportion of TEEC or TGC greater than 25% is needed to attain a modulus as high as those of the standards.

Fig. 4.21

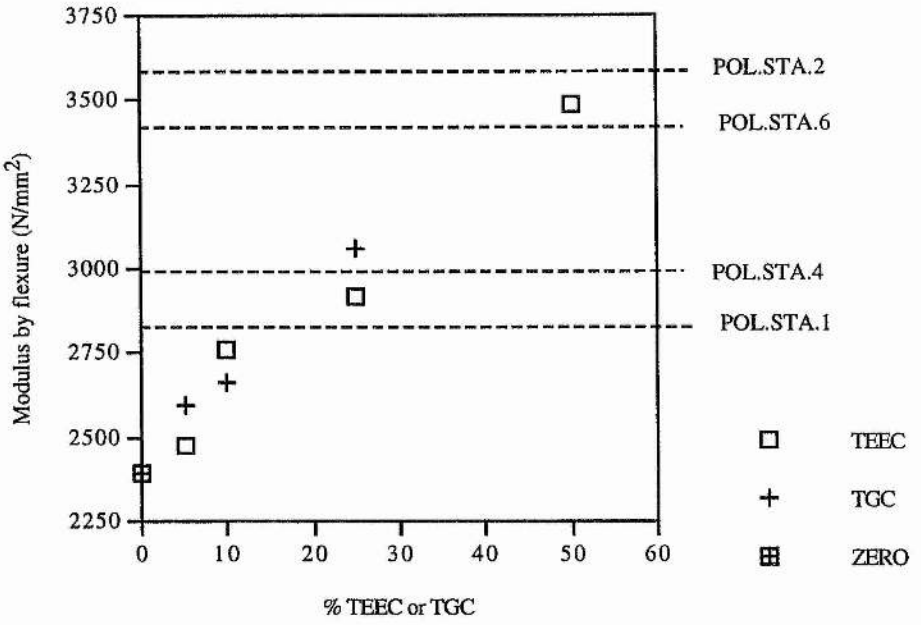
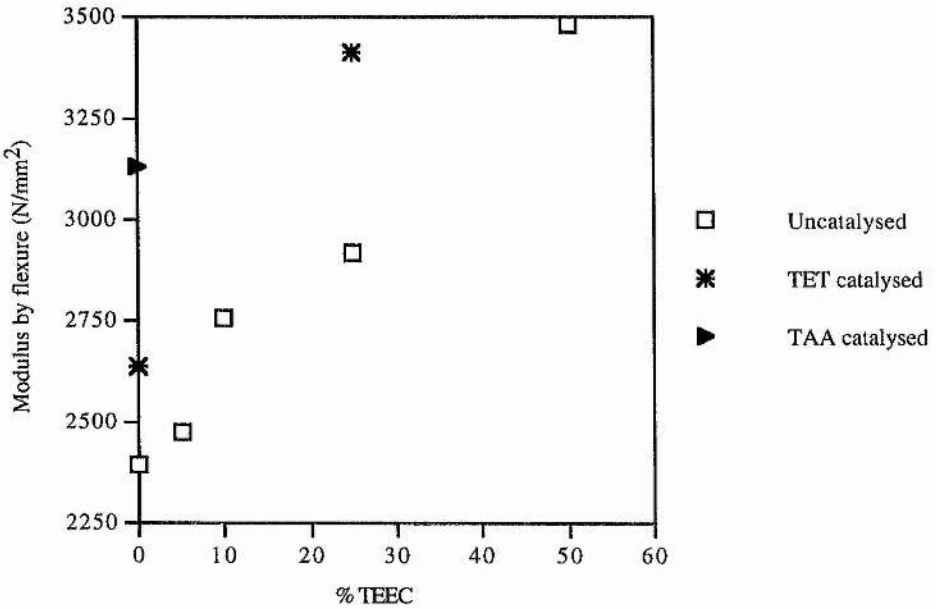


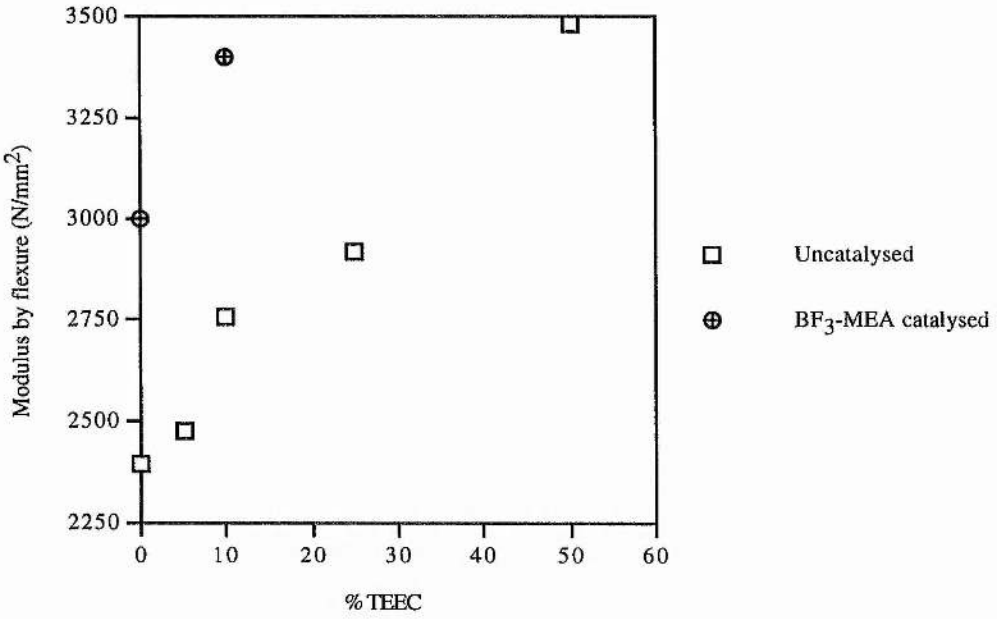
Fig. 4.22



When the catalysed polymers are compared with the uncatalysed ones (Fig. 4.22 above) it is seen that the more reactive catalyst (TILCOM TAA) gives a polymer of much higher modulus (POL.TEEC/TGC.0.TAA) than the uncatalysed analogue (POL.TEEC/TGC.0), even though it was cured at a much lower temperature (121°C as opposed to 177°C). The other catalysed polymer (POL.TEEC/TGC.0.TET) has only a slightly higher modulus than the uncatalysed analogue, but when 10% TEEC is included there is a significantly larger difference between the moduli of the catalysed and uncatalysed analogues.

When the BF_3-monoethylamine complex was added to aid curing, the modulus was increased relative to that of the same polymers cured without the catalyst, as shown in Fig. 4.23 (below).

Fig. 4.23



If an assumption is made that the modulus by flexure is increased proportionally to the degree of curing (and that any catalyst only affects this degree of curing without affecting other properties) then from these results it can be said that TILCOM TET at

121°C cures Epon 828 and DDS to a slightly greater extent than with no catalyst at 177°C, and that TILCOM TAA at 121°C and BF_3-monoethylamine complex at 177°C cure the same system to a much greater extent still. When some cyanurate-containing, epoxy functionalised, monomer is incorporated into the system then the modulus is increased further.

4.2.2.3.4 Tensile strain

It is not as straightforward to measure tensile strain as it is flexural strain, due to the fact that ordinary samples have a tendency to break in the clamp jaws of the apparatus, thus not reaching the ultimate strain value. Specially machined "dog-bone" shaped samples are required to ensure that the samples break in the middle at maximum stress (as described in experimental section 4.3). For this reason it was not possible to test all the samples, only the TEEC range of polymers (Table 4.4).

Table 4.4

Polymer	Tensile strain (%)	Standard deviation (%)
POL.TEEC/TGC.0	6.892	-
POL.TEEC.10	8.686	1.343
POL.TEEC.25	4.757	0.157
POL.TEEC.50	3.300	-

These results were averaged from three samples. Where no standard deviation is quoted results were recorded for only one sample: the others breaking in the wrong place despite the use of the "dog-bone" samples.

Fig. 4.24

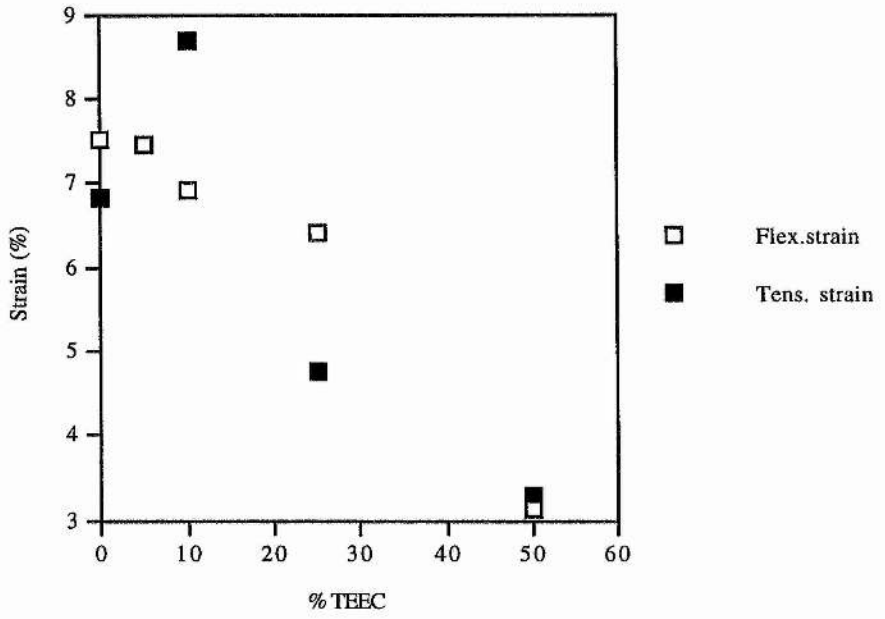


Fig. 4.24 (above) shows that, apart from the anomalous peak at 10% TEEC (POL.TEEC.10), the graph of tensile strain against percentage TEEC composition graph is quite similar to the plot of flexural strain against percentage TEEC composition, as would be expected. The strain value decreases with the amount of cyanurate incorporated in the polymer.

4.2.2.3.5 Tensile stress

Like tensile strain, (and for the same reason), tensile stress is not as easy to measure as its flexural equivalent and only the same four samples provide the results here (Table 4.5).

As in the case of tensile strain, the results were averaged from three samples, but where no standard deviation is quoted only one sample gave valid results.

Table 4.5

Polymer	Tensile stress (N/mm^2)	Standard deviation (N/mm^2)
POL.TEEC/TGC.0	65.11	-
POL.TEEC.10	76.13	8.473
POL.TEEC.25	58.03	3.026
POL.TEEC.50	56.85	-

Fig. 4.25

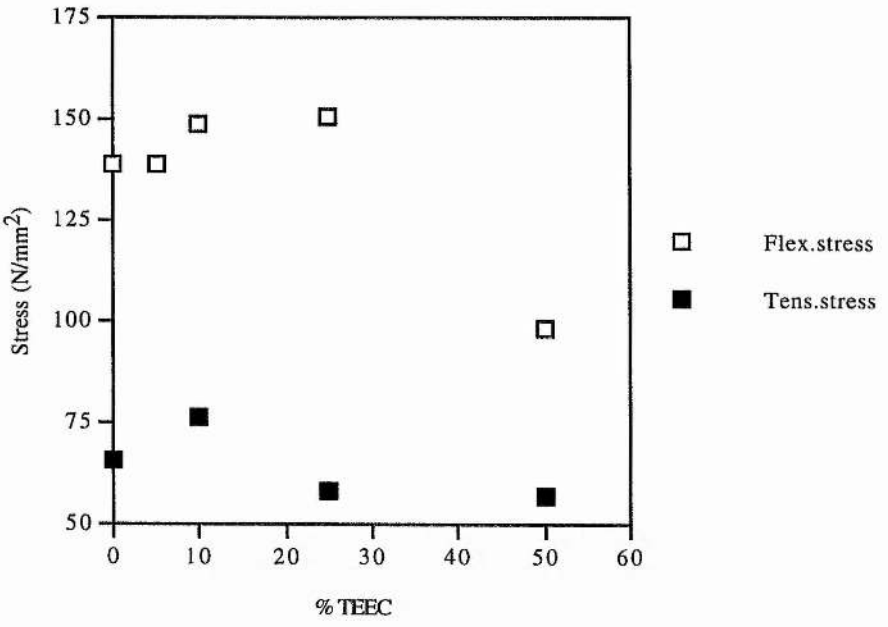


Fig. 4.25 (above) once more shows that the tensile results follow a similar pattern to the flexural ones, but the tensile values are much lower.

It is difficult to draw many conclusions from both tensile stress and tensile strain results because of the limited amount of data available. What can be said is that the

apparent trends are consistent with those observed for their flexural equivalents, as would be expected, and that therefore it would be reasonable to assume that the other polymers, including the catalysed analogues, would also fit the same trends as observed for the flexural measurements.

4.2.2.3.6 Modulus by tension

Table 4.6

Polymer	Modulus by tension (N/mm^2)	Standard deviation (N/mm^2)
POL.STA.1	1328	178
POL.STA.2	1673	72
POL.STA.3	1544	78
POL.STA.4	1589	38
POL.STA.5	1705	39
POL.STA.6	too brittle to clamp	-
POL.TEEC/TGC.0	1228	34
POL.TEEC.5	1329	56
POL.TEEC.10	1361	68
POL.TEEC.25	1467	57
POL.TEEC.50	1767	87
POL.TGC.5	1413	20
POL.TGC.10	1394	57
POL.TGC.25	1581	57
POL.TEEC/TGC.O.TET	1137	45
POL.TEEC/TGC.0.TAA	1233	*
POL.TEEC.25.TET	1521	148

* Only one result available

The difficulties experienced in measuring stress and strain by tension are not shared by the measurement of modulus this way. Modulus measurements can be taken well before the sample breaks, so as long as the second point from which the modulus parameters are taken occurs before this happens, the fracturing in the clamp jaws becomes irrelevant. Hence the specially machined "dog-bone" samples are unnecessary and the tests can be carried out on a wider range of polymers. The results are displayed in Table 4.6 (above).

Fig. 4.26

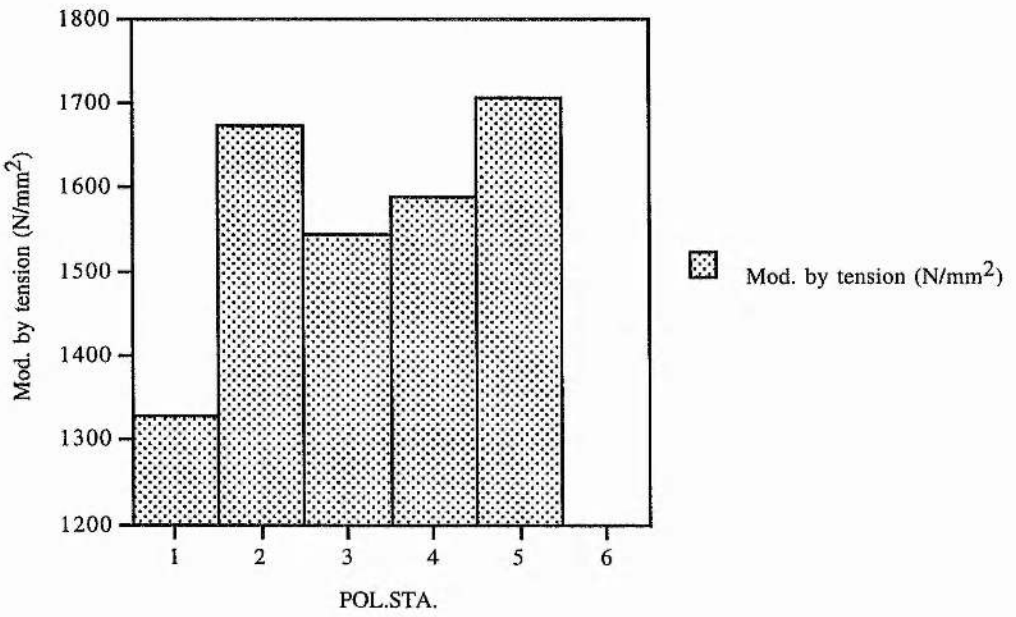
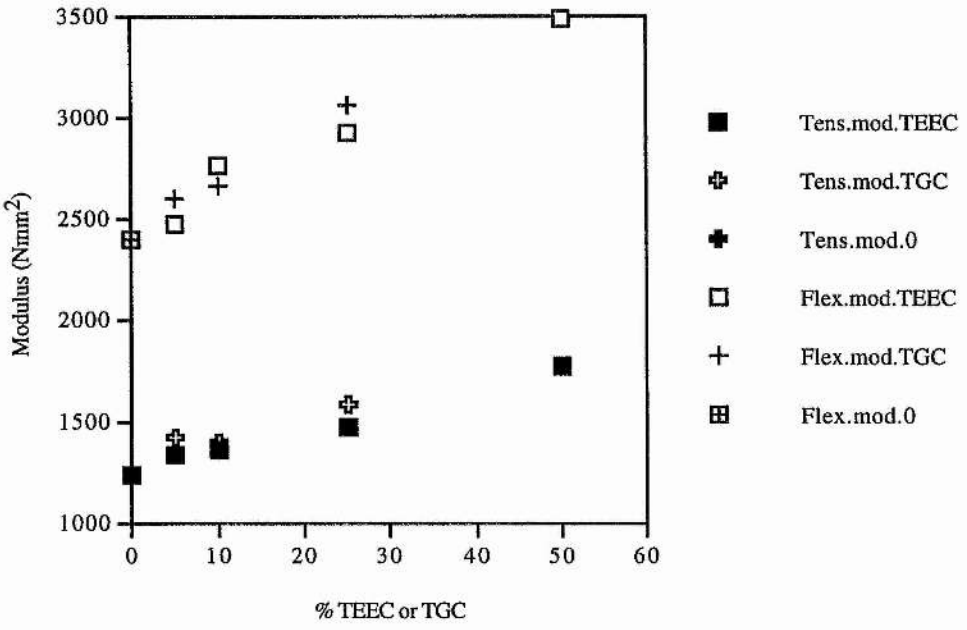


Fig. 4.26 (above) compares moduli measured by tension for the standard polymers. The pattern is very similar to that for the moduli measured by flexure, although in this case POL.STA.5 has the highest value with POL.STA.2 the next; this order is reversed for the flexural measurements.

Although the pattern is similar, the actual values of modulus are around 50% lower when measured by tension as opposed to flexure.

Next, looking at the modulus measured by tension of the TEEC and TGC ranges of polymers (Fig. 4.27 below), it can be seen that the trend is similar to that observed for the modulus measured by flexure, i.e. the modulus increases as the percentage of TEEC and TGC increases, and the polymer gets stiffer. Again the values are all consistently lower than those measured by flexure.

Fig. 4.27



It is also observed (Fig. 4.28 below) that most of these polymers have modulus values comparable to those of the standard cyanate ester resins and by the inclusion of 50% TEEC (POL.TEEC.50) a value higher than all the standards.

This is a noticeable difference from the modulus by flexure results where a TEEC or TGC content of 25% is necessary to attain values comparable to those of the standard polymers.

When the catalysed polymers are tested (Fig. 4.29 below) it is seen that, both in the case of TILCOM TET and TILCOM TAA catalysis, the moduli by tension are very similar to those of the uncatalysed analogues, for both 0% TEEC and 25% TEEC.

Fig. 4.28

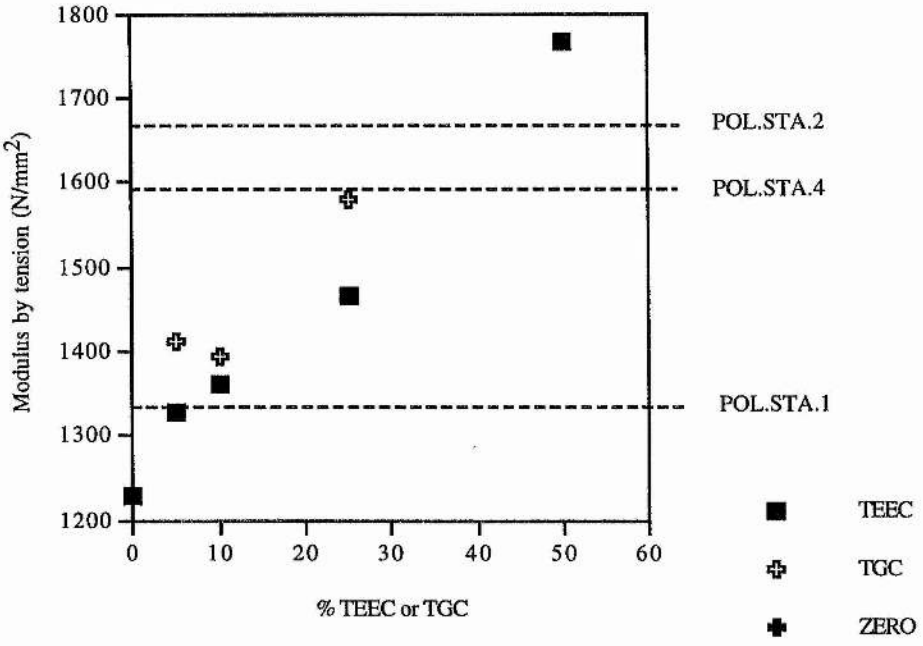
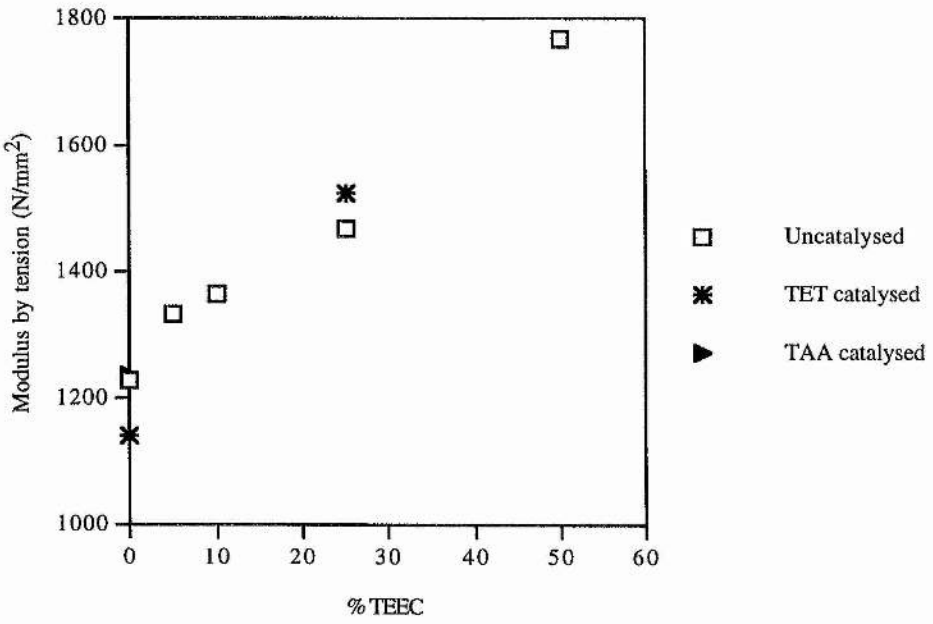


Fig. 4.29



Just as with the modulus measured by flexure, these results do not take into account any shear modulus contribution. Again the reasons are that shear modulus is a very small component, consistent in all the samples, and not affecting the *relative* moduli upon which most discussion is based at this stage.

4.2.2.3.7 Summary of mechanical testing results

In Chapter 1 the relative properties of epoxy resins and cyanate ester resins were discussed, leading to the conclusion that an improved polymer would incorporate the best properties of both systems without the drawbacks of either. Both epoxy resins and cyanate ester resins have good mechanical properties, so the most important result obtained from these mechanical testing experiments is that no detrimental effect on mechanical properties is apparently introduced by including structural units derived from the epoxy-functionalised cyanurate monomers TEEC and TGC into a standard epoxy resin. (The TEEC and TGC monomers were used as the means of obtaining these improved new polymers with the best properties of both epoxy resins and cyanate ester resins.)

Most of the polymers which include either TEEC or TGC derived units show values comparable to those of the standard polymers tested. In general, when TEEC or TGC is substituted for some of the Epon 828 in the Epon 828 / DDS system, the modulus and stress values are increased and strain values decreased. This means that increasing the amount of cyanurate makes the polymer stiffer.

Results obtained from using catalysts (especially BF_3-monoethylamine complex) to cure the same monomer mixtures suggest that the uncatalysed versions may not be fully cured. This would not affect the trends observed, but modulus and stress values would be increased and strain values decreased in catalysed systems.

Also the polymers cured with TILCOM TET and TILCOM TAA show that it is possible to cure these polymers at lower temperatures and maintain good mechanical properties, one of the main demands of this research.

Another advantage is the "tunability" of these polymers. It is possible to carry out the curing at different temperatures for different times and using different catalysts, and, it appears that the mechanical properties can be chosen by picking the appropriate amount of epoxy-functionalised cyanurate to replace some of the Epon 828 (or other epoxide monomer for that matter) in the Epon 828 / DDS (or indeed other curing agent) mixture for the desired curing conditions. This might make the polymers useful for a variety of applications. However, a larger series will have to be tested to establish the generality of the trends.

4.2.2.4 Fracture mechanics

This work was carried out by the Mechanical and Tribological Properties Workgroup in the Characterisation, Analytical and Polymer Science Group at ICI Wilton. Only two polymers were tested due to financial restrictions. Of these two polymers one contained 10% TEEC and the other no TEEC to attempt to discover whether the inclusion of TEEC affected the fracture toughness.

Table 4.7

Polymer	K_c ($MNm^{-3/2}$)	G_c ($kJ\ m^{-2}$)
POL.TEEC/TGC.0.BF_3	0.93 (0.25)	0.34 (0.17)
POL.TEEC.10.BF_3	1.00 (0.28)	0.35 (0.18)

(Figures in brackets are the standard deviations).

The results shown in Table 4.7 (above) appear to show that both polymers have a very similar toughness with POL.TEEC.10.BF_3 (the cyanurate containing polymer) being slightly tougher as would be expected. [It was revealed (*cf.* Chapter 1, p.7) that epoxy resins have a greater propensity to microcrack than cyanate ester resins, and the

cyanurate based monomer (TEEC) is incorporated in an attempt to bring cyanate ester resin character to the epoxy resin system.] However, as well as there being doubts over the accuracy of these results, due to the high standard deviations, the results indicate that it is impossible to differentiate between the two materials by this analysis. According to D.S. Smith of the Mechanical and Tribological Properties Workgroup in the Characterisation, Analytical and Polymer Science Group at ICI Wilton, this is because the plastic zone radius at the crack tip is of the same order as the crack tip radius (i.e. approaching 1μm), and the precision of the analysis becomes worse as the plastic zone decreases below 10μm and nears 1μm, reducing the value for K_c. Even so, the values for G_c and K_c are very similar to ones quoted in a private communication[44] for the same Epon 828 / DDS polymer cured with BF_3-monoethylamine complex (POL.TEEC/TGC.0.BF_3).

It is not yet possible to determine whether adding epoxy-functionalised cyanurate monomers to an epoxy system will improve the microcrack resistance to a level approaching that of a cyanate ester resin.

4.2.2.5 Glass transition temperature

Table 4.8

Polymer	T_g Processes (°C)		
	Dynamic modulus	Loss modulus	Tan δ
POL.TEEC/TGC.0	186	202	212
POL.TEEC.5	157	174	187
POL.TEEC.10	150	166	181
POL.TEEC.25	140	157	173
POL.TEEC.50	138	161	178
POL.TEEC/TGC.O.TET	124	141	154
POL.TEEC/TGC.0.TAA	130	150	168
POL.TEEC.25.TET	110	125	141

Glass transition temperatures (T_g's) were calculated from dynamic mechanical thermal analysis (DMTA) of polymer samples carried out by the Thermal Analysis Group in the ICI Wilton Characterisation and Measurement Facility. Values were given for three T_g processes; Dynamic Modulus E' (onset); Loss Modulus E" (peak); Tan δ (peak) as described in Table 4.8 (above).

(For further details of the precise physics involved see ref.45). In DMTA a sinusoidal stress is imparted to a sample. As the polymer is heated through its glassy state to its rubber-like state the way it responds to this stress changes. In this way the T_g can be identified in different ways. The dynamic modulus method defines the T_g as the onset of the decrease in stored energy as it goes through a point of inflexion. The loss modulus T_g is defined as the peak in energy dissipated by the material. The tan δ T_g is defined as the peak of the damping energy in the system which is related to the internal friction.

Figs. 4.30, 4.31 and 4.32 (below) show the T_g values plotted against the TEEC content of all the polymers for each of the three T_g processes.

Fig. 4.30

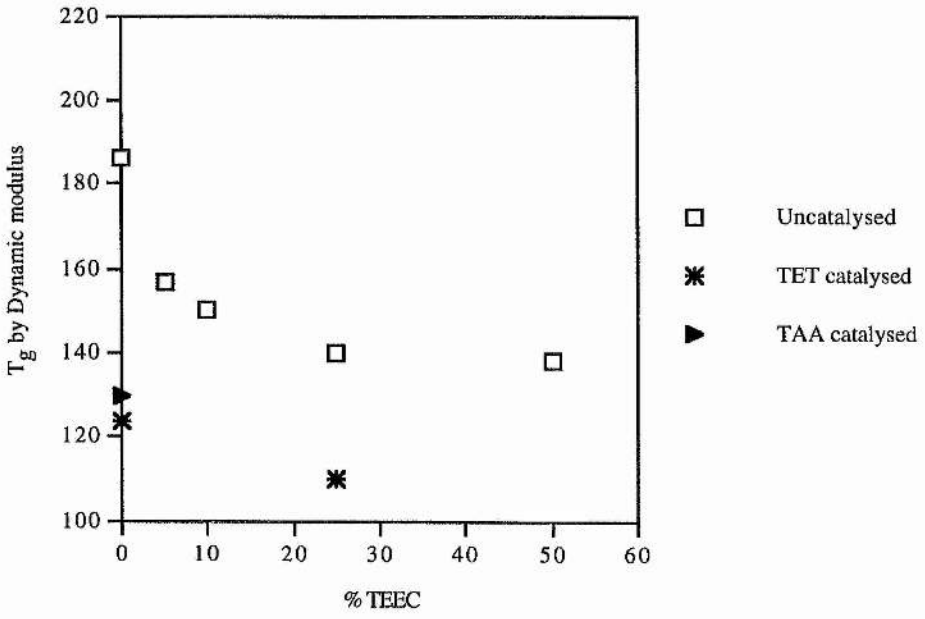


Fig. 4.31

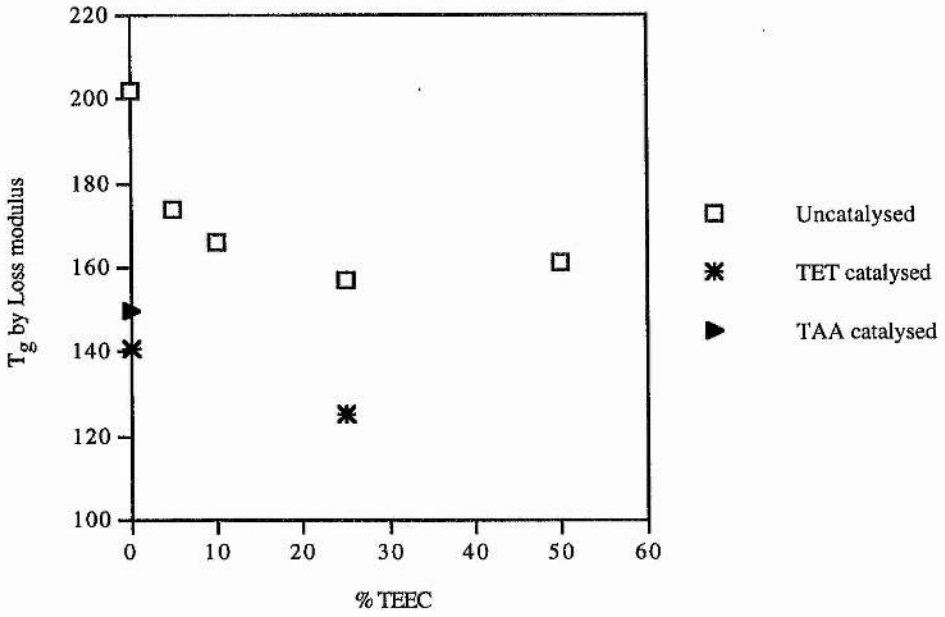
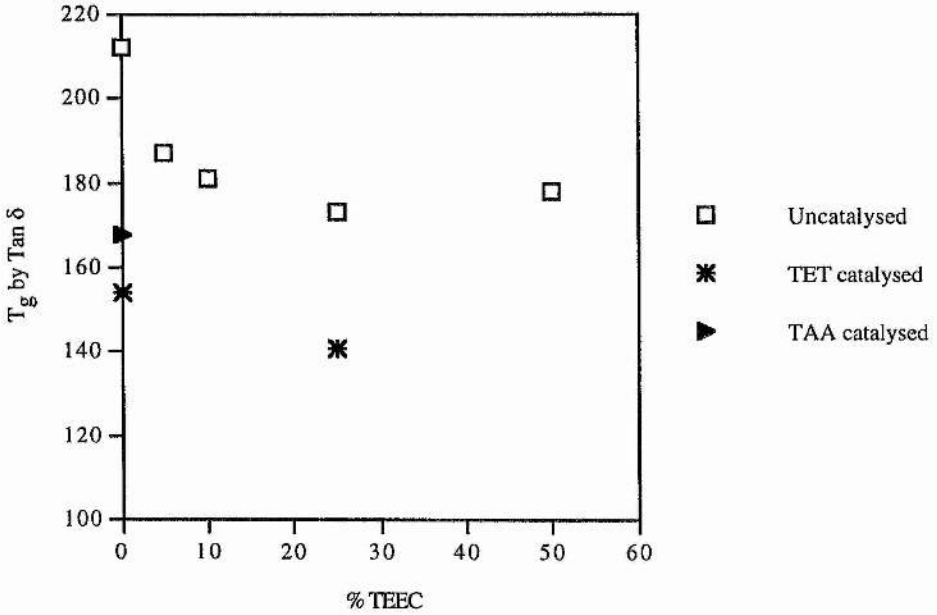


Fig. 4.32



All three graphs show a similar trend in that the T_g decreases as the TEEC content increases, levelling out somewhat above 25% TEEC. This is not what was expected, rather the opposite, because increasing the amount of TEEC was expected to increase the amount of cross-linking, which generally results in an increase in T_g. This leads to the conclusion that perhaps the degree of cure is reduced as the amount of TEEC is increased, with the TEEC epoxy groups being less reactive than the Epon 828 ones. However, there is no obvious reason why this should be the case. Furthermore, the presence of the triazine nitrogen atoms in TEEC might, if anything, increase the amount of cross-linking through the possible action of these as tertiary amine curing agents.

The TILCOM TAA and TILCOM TET catalysed polymers also show this trend and have significantly lower T_g's still, leading to the conclusion that they are cured to an even smaller extent. This, however, is not in agreement with some of the mechanical testing results. If, with more TEEC present, the extent of curing was less and the T_g lower, then flexural strain would be expected to increase and the modulus would be expected to decrease, when in fact the opposite was observed.

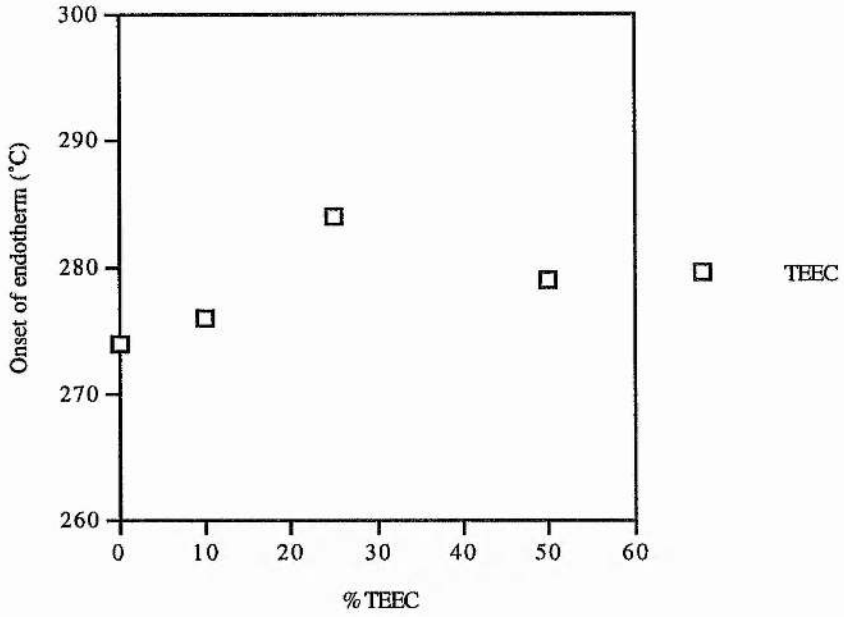
Differential scanning calorimetry (DSC) experiments were also carried out, but these only led to further confusion. The only heat changes observed were of an endothermic nature but were by no means "classic" points of inflexion. The results are tabulated in Table 4.9 (below).

Table 4.9

Polymer	Onset of endotherm (°C)
POL.TEEC/TGC.0	274
POL.TEEC.10	276
POL.TEEC.25	284
POL.TEEC.50	279

Fig. 4.33 (below) shows how this endotherm point varies with the amount of TEEC present.

Fig. 4.33



Here no regular trend is observed, although all the TEEC-containing polymers show the endotherm at a higher temperature than the standard polymer. The temperatures are completely different from T_g values obtained using DMTA, and so may not actually be due to the glass transition. Also noted from the DSC scans is the fact that no noticeable exotherm typical of a curing reaction is observed.

If it is assumed that the DMTA T_g's are correct and that the level of curing in each of the uncatalysed TEEC-containing polymers is the same, then it can be concluded that the inclusion of the epoxy functionalised cyanurate into an epoxy resin system has a negative effect on the T_g. This is a drawback when the original aim of the research is considered. It may be, in polymers of this type, that a combination of the better properties of epoxy resins and cyanate ester resins without the disadvantages of either may be achieved only at the expense of a high T_g. However, it is possible that slightly longer curing may lead to a more complete conversion and "respectable" T_g values.

4.2.2.6 Water absorption

Fig. 4.34

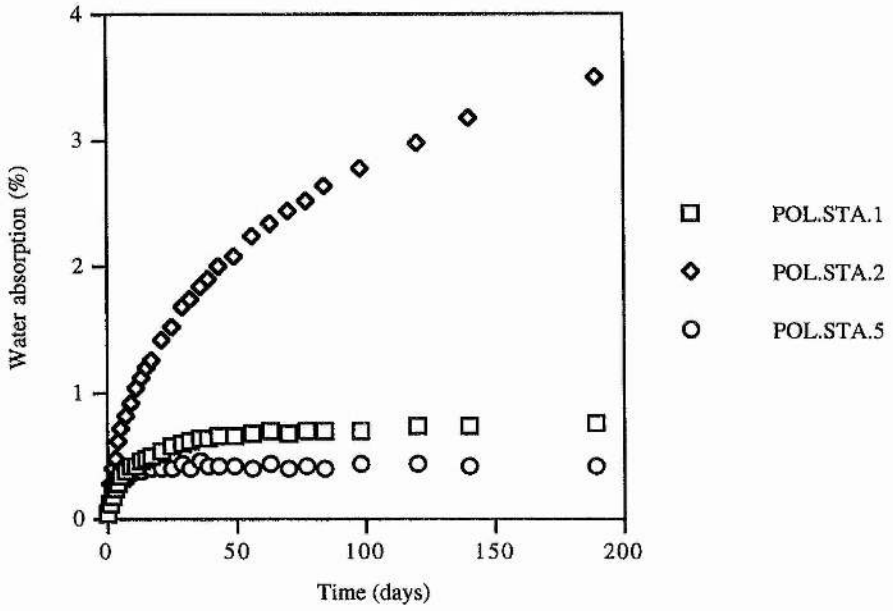
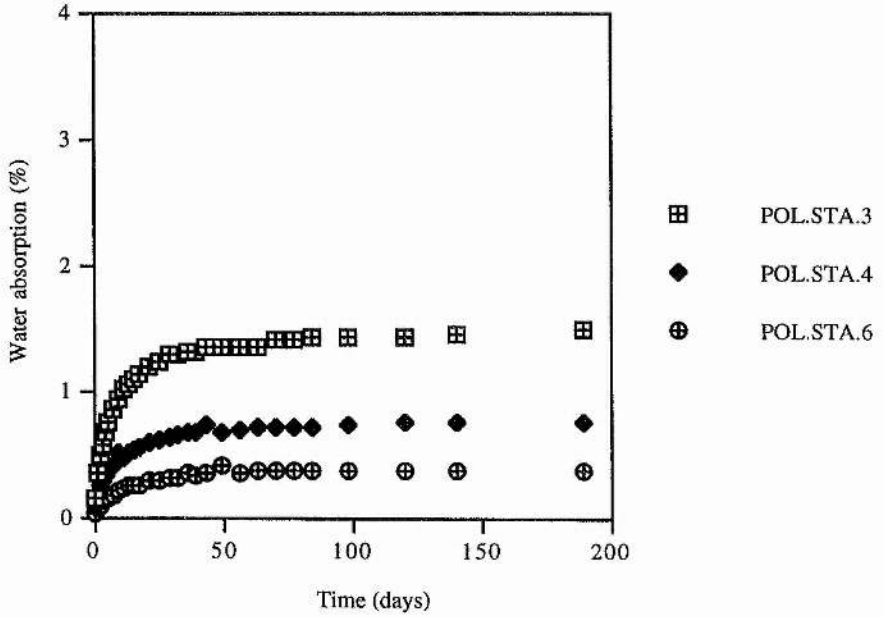


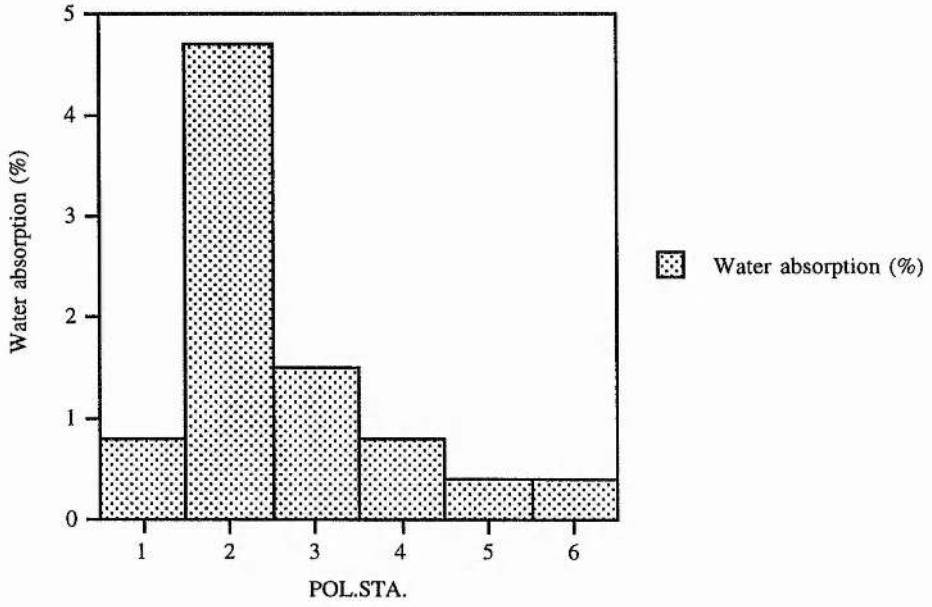
Fig. 4.35



For the six standard polymers (Figs. 4.34 and 4.35 above) the percentage of water absorbed by weight can be plotted against time. (Two figures are used for clarity as some of the plots overlap).

After 100 days had passed, the cyanate esters had all absorbed their maximum amounts of water. However, even after 200 days the epoxy resin (POL.STA.2) was still absorbing water. Extrapolation of the graph was required to provide an ultimate value for its water absorption. These ultimate values are compared in Fig. 4.36 (below).

Fig. 4.36



The epoxy resin has by far the highest water uptake percentage, around three times higher than the highest cyanate ester resin value. The lowest values are for POL.STA.5 and POL.STA.6, these being derived from the same cyanate ester monomer cured at 177°C and 121°C respectively, so the cure temperature is apparently irrelevant in the case of this polymer. However, POL.STA.3 and POL.STA.4 are also based on the same monomer, the differences being that POL.STA.3 was post-cured at 240°C and

POL.STA.4 was prepared from a 30% advanced prepolymer, and in this case the ultimate water absorption is markedly different. This leads to the conclusion that whether or not the degree of curing affects the water absorption depends on the individual monomer.

If the TEEC-containing compounds are now considered (Fig. 4.37 below) it can be seen these too are still absorbing water after 200 days. The same applies to the TGC containing polymers as can be seen in Fig. 4.38 (below).

If these plots are extrapolated, ultimate values for water absorption can be obtained and plotted against the percentage of TEEC or TGC in the epoxy component of the monomer mixtures (Fig. 4.39 below).

Fig. 4.37

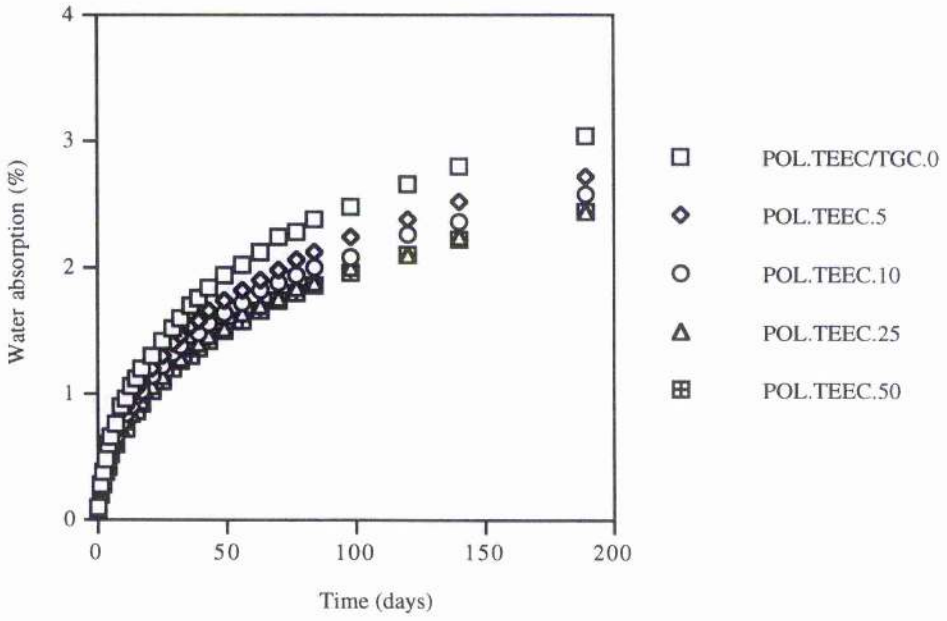


Fig. 4.38

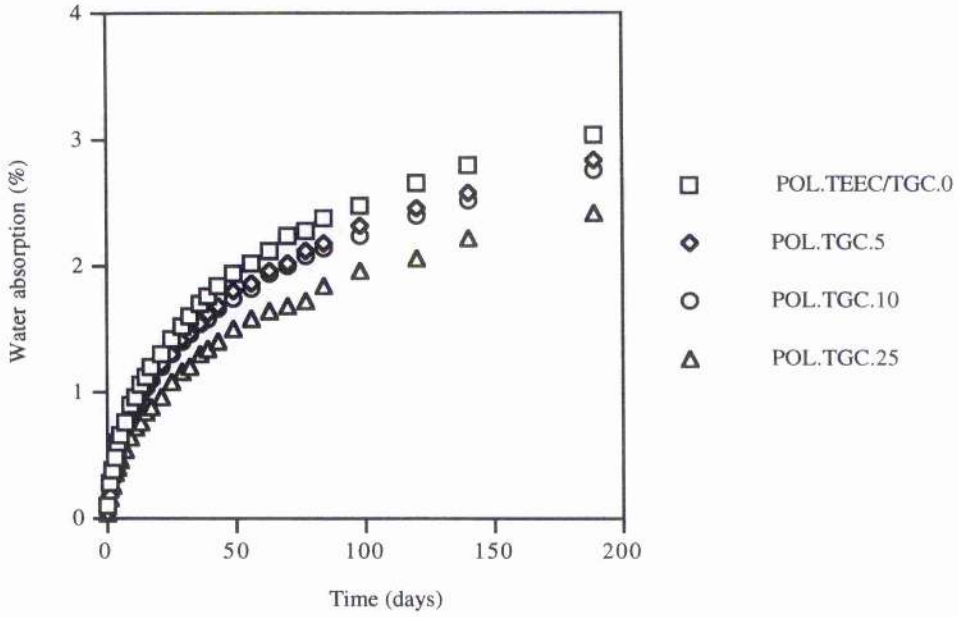
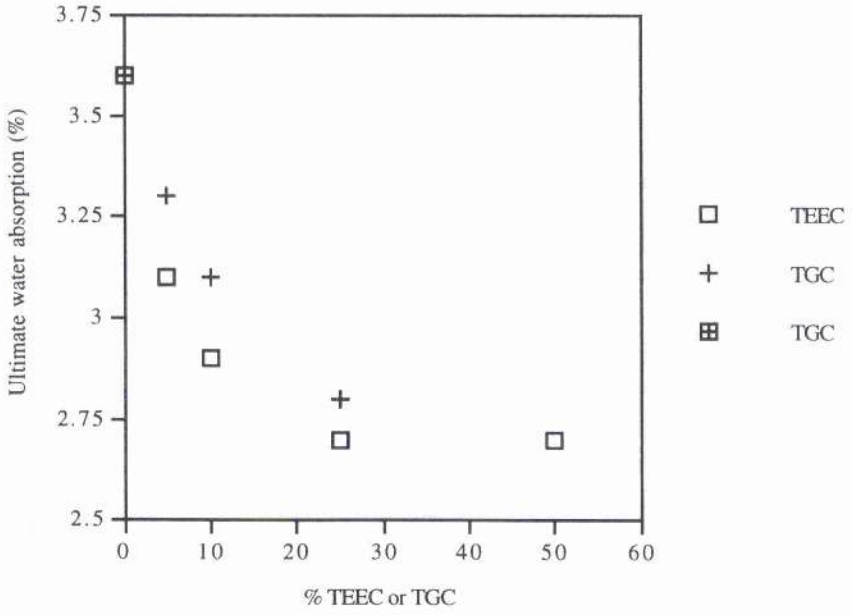


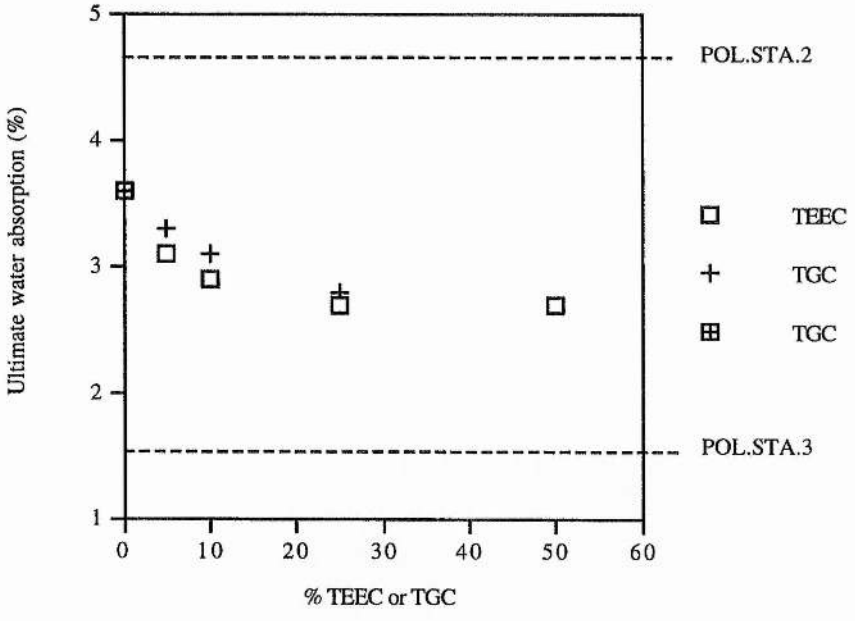
Fig. 4.39



In both cases the water absorption decreases in proportion to the percentage of cyanurate monomer included, with the effect becoming less as the amount of cyanurate monomer is further increased, and with the TGC-containing polymers absorbing slightly more water than their TEEC counterparts. This trend, *viz.* less water absorption when more cyanurate monomer is present, is what was expected, considering that for the standard polymers the epoxy resin absorbs much more water than the cyanate ester resins.

When the POL.STA.2 and POL.STA.3 values are compared with the TEEC- and TGC-containing polymers, it can be seen (Fig. 4.40 below) that the TEEC- and TGC-containing polymers have values higher than the highest water-absorbing cyanate ester resin (POL.STA.3), but lower than the epoxy resin (POL.STA.2).

Fig. 4.40



When these polymers were taken out of the water and heated at 80°C, after one week their weight was within ± 0.2% of the original dry weight. After a further two

weeks they were still within ± 0.2% of this original dry weight, therefore the absorption of water is reversible and is not a chemical reaction.

In Chapter 1 it was stated that the objective of this research was to find a way to incorporate the best properties of epoxy resins and cyanate ester resins into one system without the drawbacks of either. One advantage of cyanate ester resins is that they absorb less water than epoxy resins. These water absorption tests show that the amount of water absorbed by an epoxy resin can be reduced by incorporating some epoxy functionalised cyanurate monomers (e.g. TEEC or TGC) into the epoxy resin system, which is indeed what they set out to achieve. Also, it has been shown that any water absorption that does take place is readily reversible.

4.2.2.7 Dielectric measurements

Dielectric measurements were carried out at Strathclyde University at both high and low frequencies; however, only the low frequency results are quoted here. The high frequency results had errors that could not be corrected by scaling and the opinion was offered by the tester that "they would be so hedged around with qualifications as to be useless", apparently due to the dimensions of the samples available.

Four polymers, *viz.* POL.TEEC/TGC.0, POL.TEEC.10, POL.TEEC.25 and POL.TEEC.50, were tested across a low frequency range. This was in an attempt to reveal any trends which might be induced by the increase in the proportion of epoxy functionalised cyanurate in the monomer mixture.

Fig. 4.41 (below) shows that all four polymers show a similar pattern of decreasing dielectric constant with increasing frequency. All three TEEC-containing polymers have significantly lower dielectric constants (irrespective of frequency) than POL.TEEC/TGC.0, the cyanurate-free analogue.

However, as can be seen in Fig. 4.42 (below), they are not in the expected order, which was that the greater the amount of cyanurate the lower the dielectric constant. Why POL.TEEC.10 should have lowest dielectric constant is not readily apparent.

Fig. 4.41

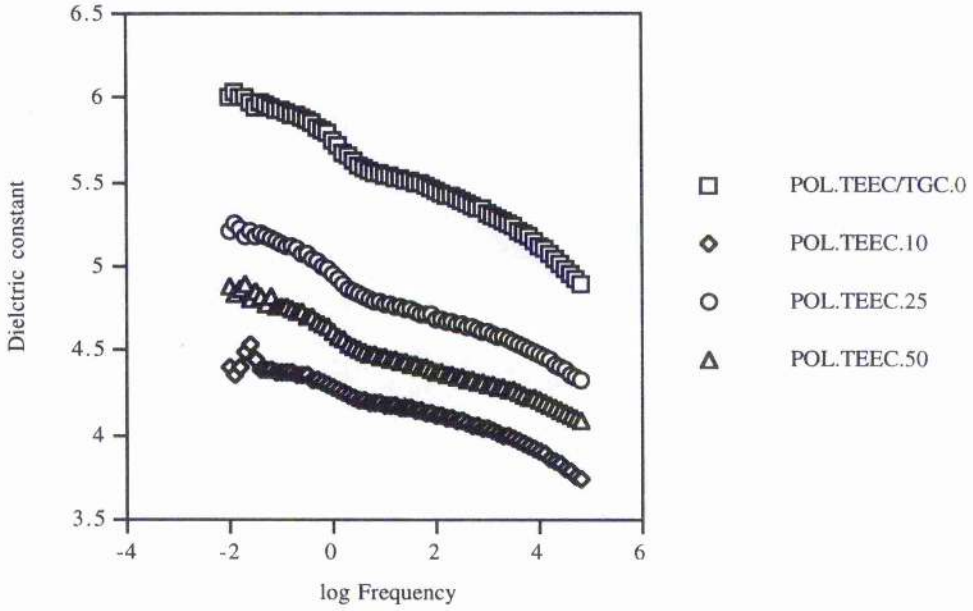
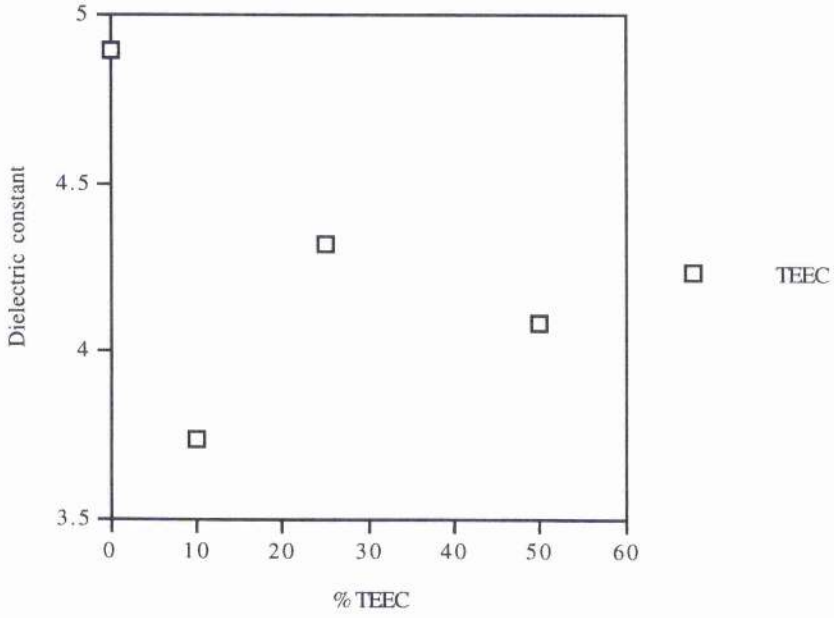


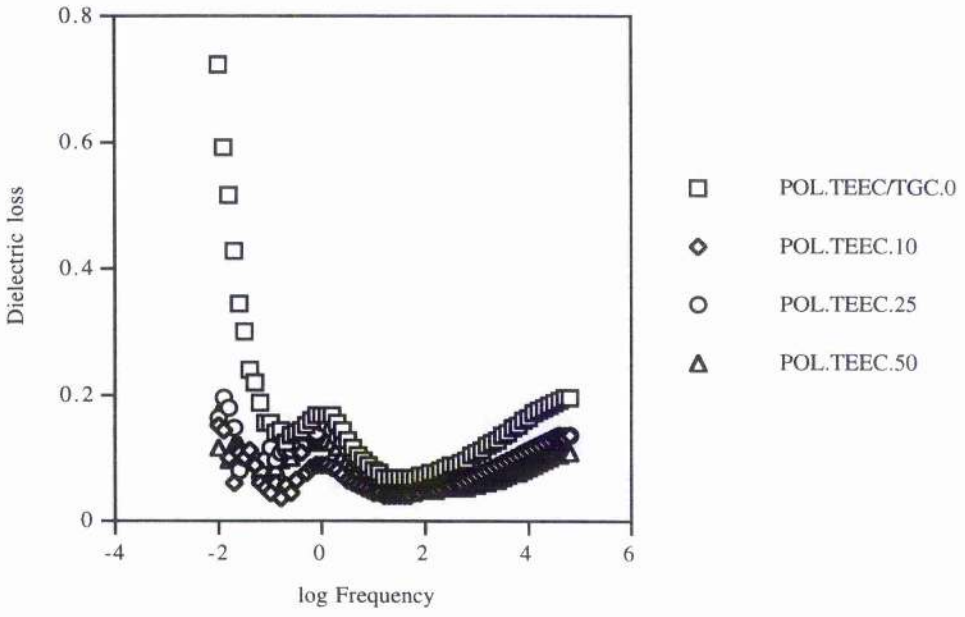
Fig. 4.42



The values for dielectric constant in Fig. 4.42 (above) are taken arbitrarily from the highest frequency measurement (frequency = 63 kHz, log frequency = 4.8) for the purposes of examining the trend. (The actual values being less important than the trend.) However, it must be emphasised that this trend might change at higher frequencies, so care must be taken not to draw too many firm conclusions.

All four polymers also show a dispersion amplitude at around 1 Hz (log frequency = 0) (Fig. 4.41). This is due to a relaxation in the chemical structure of the polymer at this frequency. It can also be seen that this relaxation is less pronounced for POL.TEEC.10 than for the others. It is likely that this is a short-range relaxation rather than the long-range bulk relaxation of the polymer. It seems that there is something anomalous about POL.TEEC.10 that makes its dielectric characteristics different from what would be expected, although it should be noted that it does not give anomalous results in the testing of other properties.

Fig. 4.43



Dielectric loss measurements show a peak at around 1 Hz (log frequency = 0) (Fig. 4.43 above). This is due to the same relaxation shown by the dispersion amplitudes in the dielectric constant plots.

Fig. 4.44

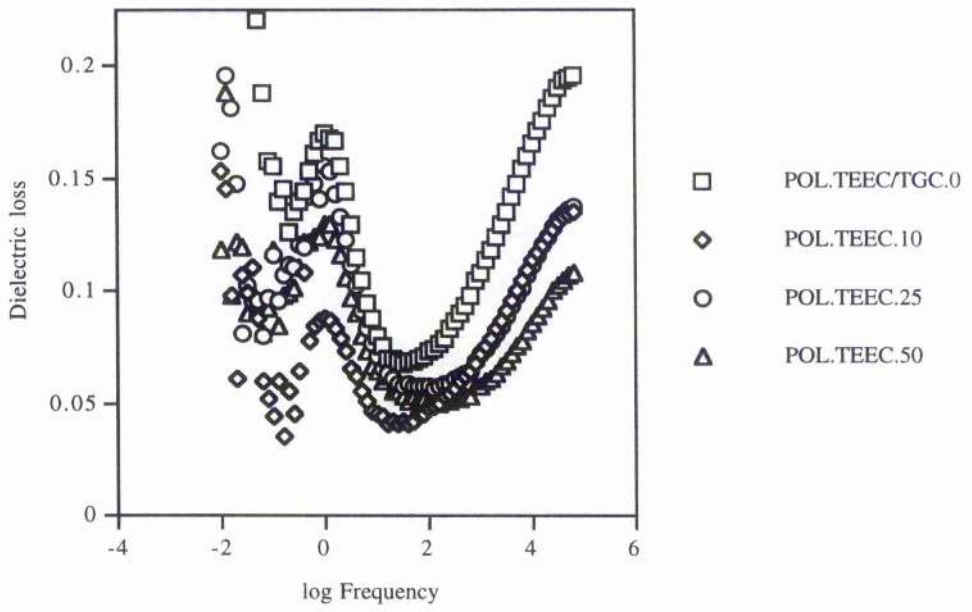


Fig. 4.44 (above) is an expanded version of Fig. 4.43 (above). The reason that the points below log frequency = 0 are very scattered is due to the fact that the limits of the experiment have been exceeded. It can be seen that, unlike the dielectric constant graphs, the dielectric loss graphs actually cross so it is not sufficient just to pick one frequency at which to correlate the four polymers' dielectric loss with their TEEC content. Fig. 4.45 (below) shows dielectric losses measured at frequency 25 Hz (log frequency = 1.4) and Fig. 4.46 (below) shows dielectric losses measured at frequency 63 kHz (log frequency = 4.8).

Fig. 4.45

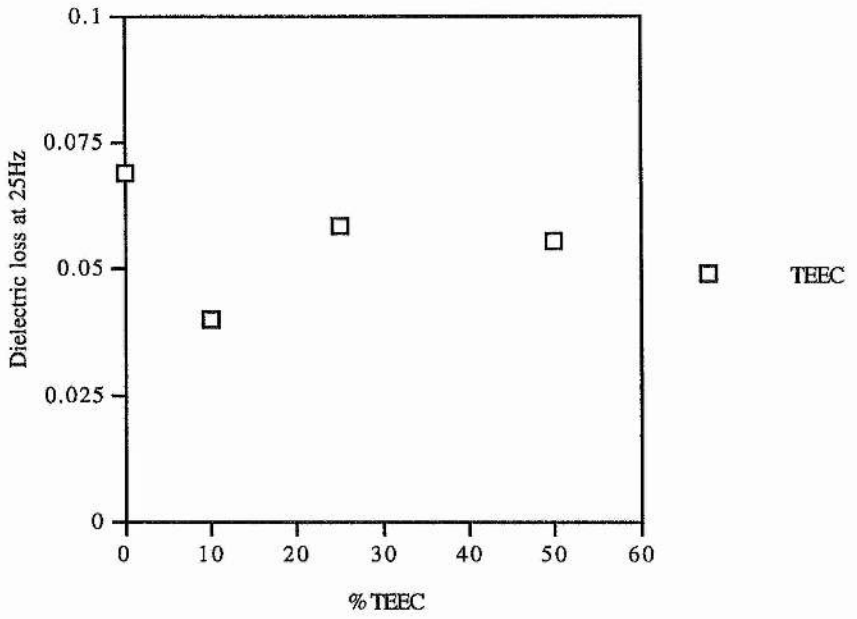
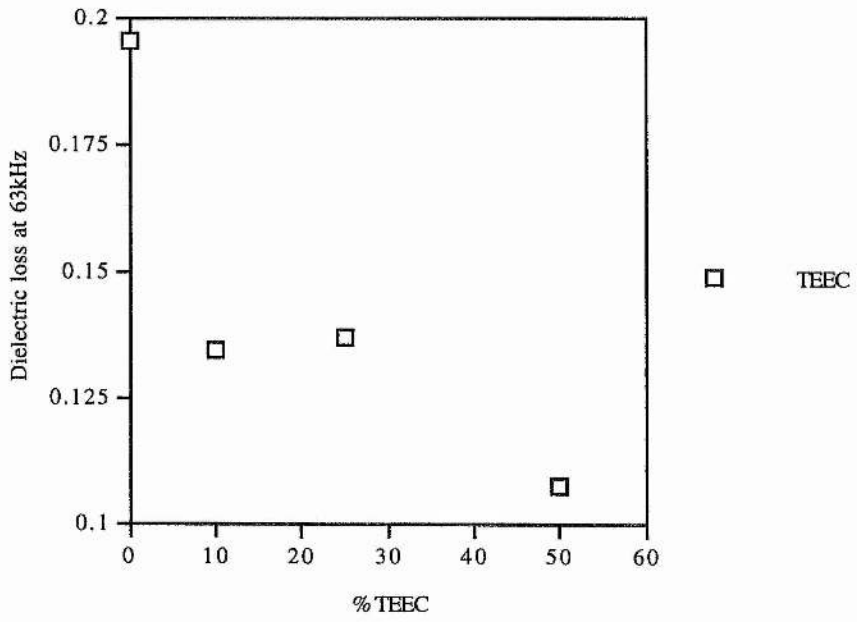


Fig. 4.46



Once more a general trend is observed, with dielectric loss decreasing with the amount of cyanurate monomer included, but again POL.TEEC.10 stands out as an anomaly, even if less so at higher frequencies. However, the objective set out at the start has been fulfilled, in that in this polymer system the dielectric properties of an epoxy resin can be improved by incorporating a degree of cyanate ester resin character through inclusion of some cyanurate-containing structural units.

4.3 Experimental

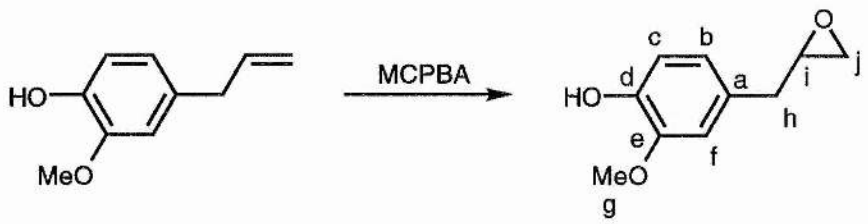
4.3.1 Monomer synthesis

Eugenol epoxide

Eugenol epoxide had previously been synthesised on a small scale by reaction of *m*-chloroperoxybenzoic acid (MCPBA) with eugenol[46], the work-up using potassium fluoride to precipitate any MCPBA or *m*-chlorobenzoic acid left. Purification was by preparative thin layer chromatography but no yields are mentioned. It was felt that this route was not desirable due to the use of potassium fluoride which would lead to the production of hydrogen fluoride and that the purification by preparative thin layer chromatography would not be ideal when comparatively large amounts of product are required.

MCPBA oxidations of double bonds are well known and the following procedure (outlined in Fig. 4.47 below) was based on one of these.

Fig. 4.47



Eugenol (60 g, 0.36 mol) was dissolved in dry dichloromethane (~100 cm^3). 55% MCPBA (200 g, 0.64 mol) was dissolved in dichloromethane and the solution then washed with water. The dichloromethane layer was separated and dried ($MgSO_4$). The dry solution of MCPBA in dichloromethane was then slowly added to the eugenol solution over 2 h keeping the temperature below 20°C. The mixture was stirred at room temperature for 48 h, then filtered to remove the *m*-chlorobenzoic acid that had

precipitated out. Excess peroxy-acid was destroyed by washing with 10% sodium metabisulfite solution, and this was followed by further washing with 10% sodium bicarbonate solution and saturated sodium chloride solution and drying over $MgSO_4$. The solvent was then evaporated off to leave a reddish liquid. Due to the reactive nature of the epoxy group it was not feasible to purify the product by distillation so column chromatography on silica gel was preferred. A 4 : 1 mixture of petroleum (b.p. 40-60°C) and diethyl ether was used as eluant, the first fraction being identified as unreacted eugenol. Once the epoxy eugenol fraction started to come off the column, the mixture proportions were changed to 7 : 3 petroleum to diethyl ether. This resulted in a yellow liquid; yield 37 g (56%). δ_H ($CDCl_3$) 2.56 (1H, dd, H_a), 2.79 - 2.83 (3H, m, CH_2 + H_b), 3.12 - 3.16 (1H, m, H_c), 3.87 (3H, s, OMe), 5.72 (1H, br s, OH), 6.72 - 6.76 (2H, m, Ar-H), 6.83 - 6.87` (1H, m, Ar-H). $J_{a,b} = J_{b,c} = J_{CH_2,c}$ 5.1; $J_{a,c}$ 2.6*. δ_C 38.4 (j), 46.9 (i), 52.8 (h), 55.9 (g), 111.6 (f), 114.4 (c), 121.6 (b), 129.0 (a), 144.4 (d) and 146.5 (e).

Other reaction conditions were used: increased temperature, various reaction times and different excesses of MCPBA, but these led to decreased yields of eugenol epoxide, with either less eugenol being used up or the epoxide ring-opening products being obtained.

Tris(epoxyeugenyl) cyanurate (TEEC)

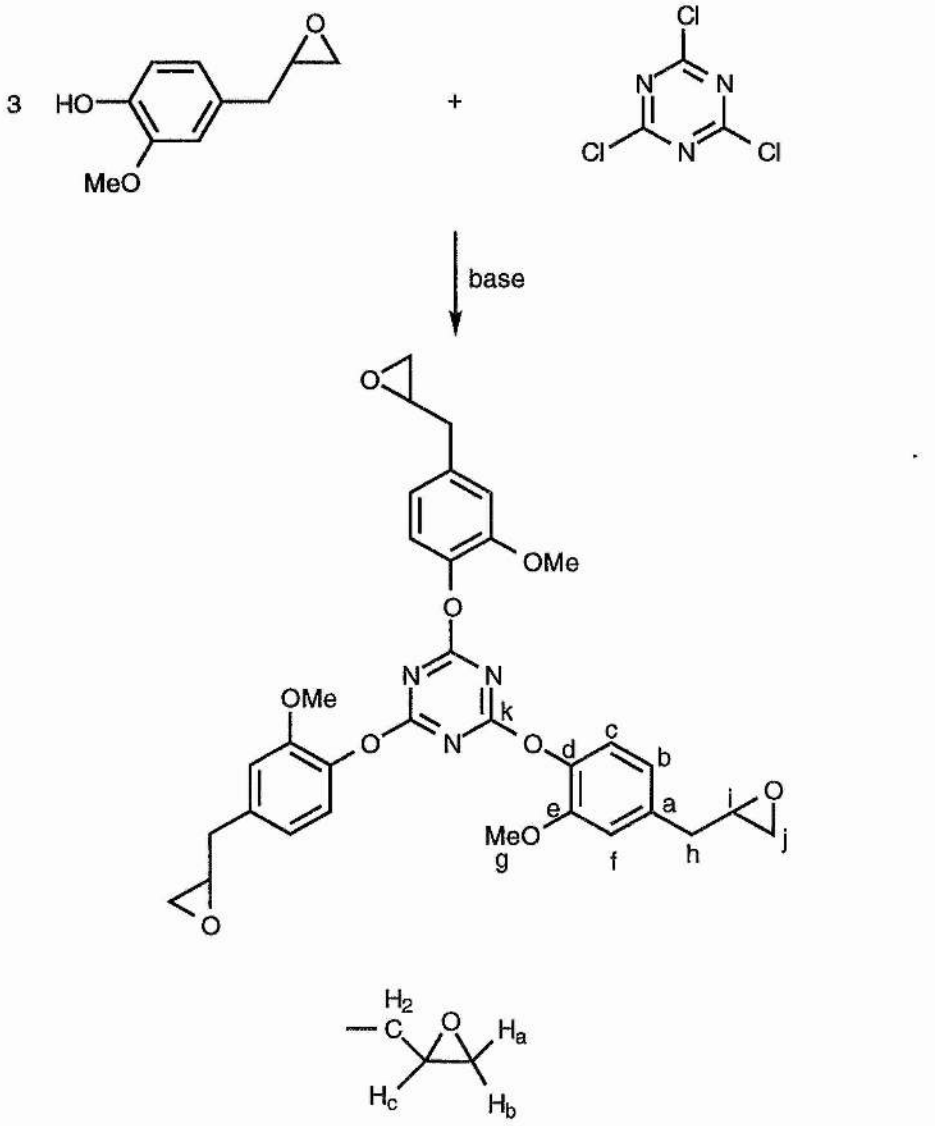
This method was adapted from a synthesis of the unepoxidised analogue in a European patent application[47].

Eugenol epoxide (18.55 g, 0.104 mol) and cyanuric chloride (6.08 g, 0.033 mol) were dissolved in acetone (~75 cm^3) and sodium hydroxide (3.95 g, 0.100 mol) in water (50 cm^3) slowly added without allowing the temperature to rise above 10°C. The mixture was then stirred for 1 h, extracted with dichloromethane and the extract dried ($MgSO_4$). On evaporation of the solvent a clear viscous liquid was obtained. This liquid was induced to recrystallise by heating with methanol, to give rosette-like

* These assignments correspond to those for TEEC (see p.115), which were derived from decoupling experiments.

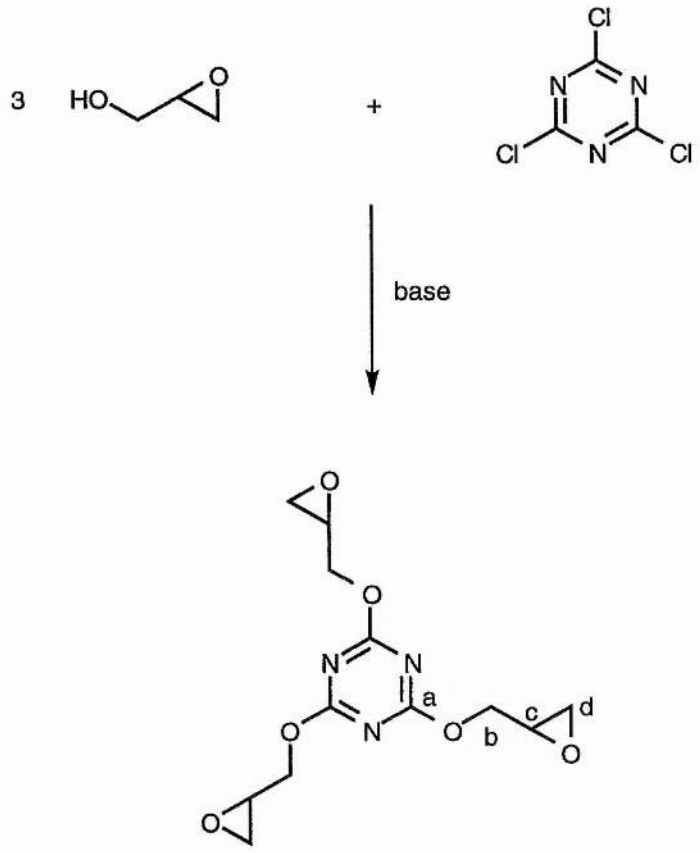
crystals, m.p. 132-134°C. Yield 17.02 g (85%). (Found: C, 64.3; H, 5.4; N, 7.0. $C_{33}H_{33}N_3O_9$ requires C, 64.4; H, 5.4; N, 6.8%.) δ_H ($CDCl_3$) 2.56 (1H, dd, H_a), 2.79 - 2.83 (3H, m, CH_2 + H_b), 3.12 - 3.16 (1H, m, H_c), 3.74 (3H, s, OMe), 6.78 - 6.82 (2H, m, Ar-H) and 7.01 - 7.05 (1H, m, Ar-H). $J_{a,b} = J_{b,c} = J_{CH2,c}$ 5.1; $J_{a,c}$ 2.6. (The assignments of the resonances of H_a, H_b, H_c and the CH_2 group, and the coupling constants, were assigned by a series of decoupling experiments.) δ_C 38.4 (j), 46.6 (i), 52.1 (h), 56.6 (g), 113.3 (f), 120.8 (c), 122.0 (b), 136.3 (a), 139.2 (d), 150.8 (e) and 173.5 (k).

Fig. 4.48



Triglycidyl cyanurate (TGC)

Fig. 4.49



The method (adapted from a U.S. patent[48]) for this reaction is similar to that for TEEC above, with a reaction mixture of glycidol (132 g, 1.78 mol), cyanuric chloride (100 g, 0.54 mol) in acetone (250 cm^3) and sodium hydroxide (67 g, 1.675 mol) in water (100 cm^3). The product is a viscous liquid and although literature references say it should be a white solid of low m.p., after chilling in diethyl ether, (softening at 30°C, completely melted at 53-60°C) ^{13}C n.m.r. showed that only very minor impurities were present and that further purification was unnecessary. Yield 146 g (91%). δ_H ($CDCl_3$) 2.73 (1H, dd, H_a), 2.89 (1H, dd, H_b), 3.38 - 3.42 (1H, m, H_c)†, 4.31 (1H, dd) and 4.70 (1H, dd, CH_2). δ_C 43.7 (d), 48.3 (c), 68.3 (b) and 172.1 (a).

† These assignments are based on analogy with the spectrum of TEEC (above).

4.3.2 Polymer synthesis

The following polymers were all prepared as 6 x 4 inch panels in polished metal moulds. The moulds were sprayed with a release agent such as 'Frekote' to allow easy removal of the panels from the moulds. The moulds were also levelled in the curing oven, using a spirit level, to ensure that the panels would have an even thickness. The monomer mixtures were prepared by dissolving the reactants (total mass 100 g) in the appropriate hot solvent and reducing the volume so that it would all fit in the mould.

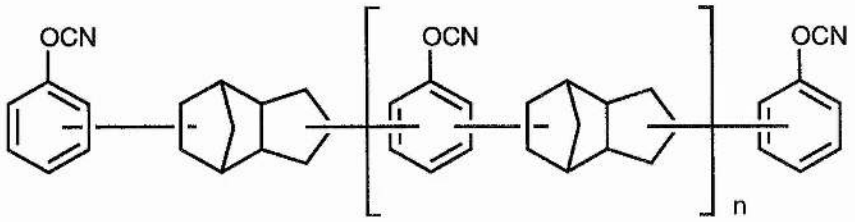
4.3.2.1 Standard polymers

Standard polymers were prepared using the manufacturer's data sheets for cure schedules.

POL.STA.1

XU 71787 cyanate ester prepolymer (Fig. 4.50) manufactured by Dow was dissolved in hot acetone and copper(II) acetylacetonate / nonylphenol catalyst (2.6 g) added. This catalyst was prepared by mixing copper(II) acetylacetonate (1 g) in nonylphenol (100 g) at 135°C for 1 h. This mixture was poured into the mould in an oven preheated to 110°C. A vacuum was carefully applied, under which conditions the acetone bubbled off. When no more degassing was observed (~ 1 h) the vacuum was released and the temperature increased to 177°C and the mixture allowed to cure at that temperature for 2 h. The black polymer was then allowed to cool in the mould slowly overnight. Once the polymer panel had been removed from the mould it was post-cured for a further 2 h at 232°C.

Fig. 4.50



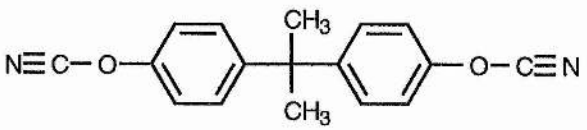
POL.STA.2

934 Epoxy (100 g), a commercially popular epoxy resin system which includes curing agents, hardeners and other additives as well as epoxy monomers, was dissolved in hot acetone. It was poured into the mould at 110°C and degassed under vacuum. The vacuum was released and the polymer cured for 2 h at 177°C.

POL.STA.3

Bisphenol A dicyanate (Fig. 4.51) (97.4 g) was dissolved in hot acetone and 2.6 g of the copper(II) acetylacetonate catalyst described in the synthesis of POL.STA.1 added. The solution was poured into the mould and degassed under vacuum at 100°C. As the solvent evaporated off the bisphenol A dicyanate crystallised out before melting later. With the vacuum released the material was cured at 177°C for 4 h. After cooling slowly overnight the polymer panel was removed from the mould and post-cured for 2 h at 240°C.

Fig. 4.51



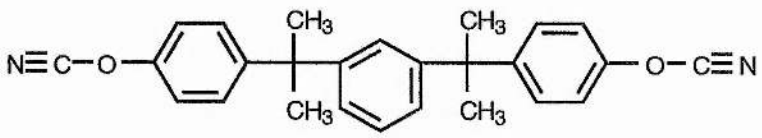
POL.STA.4

AroCy B-30 pre-polymer (97.4 g) was dissolved in hot acetone with copper(II) acetylacetonate / nonylphenol catalyst (2.6 g). AroCy B-30 is a cyanate ester pre-polymer consisting of 30% "advanced" bisphenol A dicyanate, i.e. 30% of the cyanate ester groups have already undergone reaction. This makes the oligomer a viscous liquid rather than a crystalline solid. The mixture was poured into the mould and degassed under vacuum at 100°C. Once degassing was complete the vacuum was released and the oven heated to 177°C for 3 h to give the cured polymer.

POL.STA.5

RTX 366 (Fig. 4.52) (97.4 g) was dissolved in hot acetone with copper(II) acetylacetonate / nonylphenol catalyst (2.6 g). As usual it was degassed at 100°C under vacuum then cured at 177°C for 3 h with the vacuum released.

Fig. 4.52



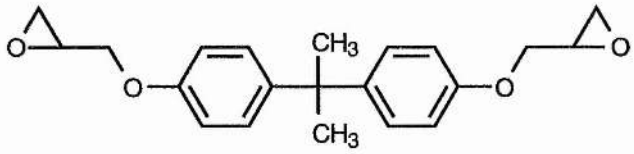
POL.STA.6

RTX 366 is claimed[49] to cure at lower temperatures than other cyanate esters. This was attempted by mixing RTX 366 (94 g) and an increased amount of copper(II) acetylacetonate / nonylphenol catalyst (6.0 g) in hot acetone. The mixture was poured into the mould and degassed under vacuum at 100°C as usual but cured at 121°C rather than 177°C for 3 h with the vacuum released.

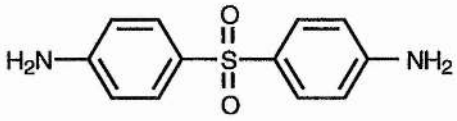
4.3.2.2 Novel polymers incorporating trisepoxyeugenyl cyanurate and triglycidyl cyanurate (uncatalysed)

These polymers are based on the curing of Epon 828 epoxy resin with 4,4'-diaminodiphenyl sulfone (DDS) as the amine curing agent (Fig. 4.53).

Fig. 4.53



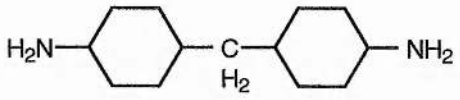
Epon 828



DDS

Trisepoxyeugenyl cyanurate (TEEC) or triglycidyl cyanurate (TGC) can be substituted in varying proportions for some of the Epon 828 and thus the effects of increasing the amount of cyanurate in the polymer can be examined. DDS requires a curing temperature of 177°C and so another amine which cures at a lower temperature would be desirable.

Fig. 4.54



Bis-(*p*-Aminocyclohexyl)methane (PACM) (Fig. 4.54) is an aliphatic amine which generally induces curing at lower temperatures than aromatic amines[50] and is also a molecule of similar size to DDS. This would help to ensure that a similar cross-link density to DDS-cured analogues would be obtained and therefore different properties would be a result of chemical differences and the lower curing temperature. These two

amines' curing with Epon 828 were checked using differential scanning calorimetry. This gave 166°C as the curing temperature for DDS and 62°C as the curing temperature for PACM.

This means that it would be difficult to use this latter amine as it may not be possible to remove all the solvent before the material starts to cure.

Reaction mixtures are calculated based on the fact that one epoxy group reacts with one amine hydrogen using Formula 4.1 below.

Formula 4.1

$$\text{Parts of amine per 100 epoxy} = \frac{\text{Amine equivalent weight}}{\text{Epoxy equivalent weight}} \times 100$$

where "amine equivalent weight" is the molecular weight of the amine per each amine hydrogen and likewise "epoxy equivalent weight" is the molecular weight of the epoxide molecule per each epoxide functionality. This then has to be recalculated for a total mass of 100 g.

In combined systems where two different epoxy monomers are mixed with an amine the formula has to be adapted as in Formula 4.2 below.

Formula 4.2

$$\text{Parts of amine per 100 epoxy} = \frac{\text{Amine eq. wt.}}{[(x / 100) \times \text{eq. wt. X}] + [(y / 100) \times \text{eq. wt. Y}]}$$

where the epoxy mixture is x% of monomer X and y% of monomer Y.

In this way the compositions of the mixtures are expressed as the percentage of epoxy groups contributed by each monomer rather than by mass of each, i.e. in a 50:50 mixture half of the epoxy groups come from one monomer and half from the other, but

it may not be a 1 : 1 ratio of the number of molecules if each monomer has a different number of epoxy groups.

POL.TEEC/TGC.0.PACM

After the application of Formula 4.1 above (and recalculation for a total mass of 100 g) Epon 828 (77 g, 0.226 mol) and bis-(*p*-aminocyclohexyl)methane (PACM) (23g, 0.110 mol) were mixed together in hot dichloromethane. (Note that the molar stoichiometry is 2:1 but, because there are two epoxy groups on Epon 828 and four amine hydrogens on PACM, the equivalent stoichiometry is 1:1). Dichloromethane was used instead of acetone as previously because of its lower boiling point, in the belief that this could enable all the solvent to be removed before curing begins. Once the mixture had been poured into the mould degassing was attempted under vacuum at 90°C; however, the polymer set solid before all the solvent had been removed and this solid had many bubbles in it.

This polymerisation was repeated with attempted degassing at 60°C under vacuum, but again was unsuccessful due to premature curing.

POL.TEEC/TGC.0

Epon 828 (74 g, 0.22 mol) and 4,4'-diaminodiphenyl sulfone (DDS) (26 g, 0.10 mol) (calculated by Formula 4.1 and adjusted for a total mass of 100 g) were mixed in hot dichloromethane with a small amount of methanol to aid dissolution of the DDS. The mixture was poured into the mould and degassed under vacuum at 110°C. Once degassing was complete the vacuum was released and the mixture heated to 177°C for three hours. The polymer was cooled overnight and removed from the mould.

After these last two polymerisation experiments it was decided to abandon the idea of using PACM as a lower temperature curing agent and concentrate on DDS.

The following polymers were all synthesised by the same method as for POL.TEEC/TGC.0 above using Formula 4.2 (with adjustments for a total mass of 100 g) to calculate amounts of monomers. Only the mixture compositions are shown below.

POL.TEEC.05

Epon 828 (69.12 g, 0.203 mol), tris(epoxyeugenyl) cyanurate (TEEC) (4.39 g, 0.007 mol) and DDS (26.52 g, 0.107 mol).

POL.TEEC.10

Epon 828 (64.87 g, 0.191 mol), TEEC (8.69 g, 0.014 mol) and DDS (26.3 g, 0.106 mol).

POL.TEEC.25

Epon 828 (52.91 g, 0.156 mol), TEEC (21.32 g, 0.035 mol) and DDS (25.76 g, 0.104 mol).

POL.TEEC.50

Epon 828 (34.08 g, 0.100 mol), TEEC (41.10 g, 0.067 mol) and DDS (24.85 g, 0.100 mol).

POL.TGC.05

Epon 828 (70.74 g, 0.208 mol), triglycidyl cyanurate (2.17 g, 0.007 mol) and DDS (27.14 g, 0.111 mol).

POL.TGC.10

Epon 828 (68.08 g, 0.200 mol), TGC (4.41 g, 0.015 mol) and DDS (27.57 g, 0.111 mol).

POL.TGC.25

Epon 828 (59.54 g, 0.175 mol), TGC (11.58 g, 0.039 mol) and DDS (28.94 g, 0.117 mol).

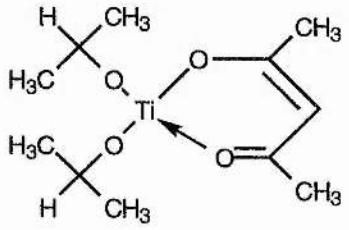
POL.TGC.50

Epon 828 (43.22 g, 0.127 mol), TGC (25.20 g, 0.085 mol) and DDS (31.55 g, 0.127 mol). In this case, as the polymer cured, fracture patterns of a circular nature began to appear. The polymer broke along some of these on removal from the mould and was unsuitable for testing.

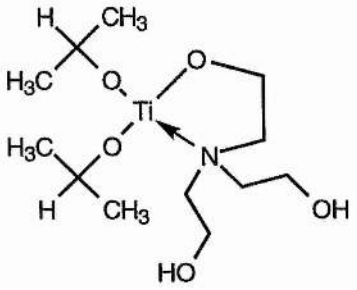
4.3.2.3 Novel polymers incorporating tris(epoxyeugenyl) cyanurate and triglycidyl cyanurate (catalysed)

Following the fact that the use of an aliphatic amine leads to curing at too low a temperature the possibility of using catalysts to lower the cure temperature of DDS was examined. The two titanium compounds below (Fig. 4.55) have been shown to possess this property[44].

Fig. 4.55



di-isopropoxytitanium acetylacetonate (TILCOM TAA)



triethanolamine di-isopropoxytitanate (TILCOM TET)

The catalysts are made up as solutions in isopropanol.

These compounds were tested using differential scanning calorimetry and compared with the two amines' curing temperatures from similar experiments (Table 4.10).

Table 4.10

Mixture	Cure Temperature (°C)
Epon 828 + DDS	166
Epon 828 + DDS + TET	130
Epon 828 + DDS + TAA	92
Epon 828 + PACM	62

From these results it can be seen that the two catalysts lower the curing temperature from that with DDS alone, but not as far as curing with PACM. This means that lower curing could be possible and that it should be possible to degas the mixtures before curing starts, especially with TILCOM TET although the use of TILCOM TAA, with the lower cure temperature, may be less straightforward.

The following polymers were again all synthesised by the same method as for POL.TEEC/TGC.0, except that the cure temperature was 121°C. Formula 4.1 was used to calculate the mixture proportions when Epon 828 was the only epoxy

compound present and Formula 4.2 used when TEEC was also included in the mixture. Again it was necessary to recalculate so that the total mass of all reactants including the catalyst was 100 g.

POL.TEEC/TGC.0.TET

Epon 828 (69.38g, 0.204 mol), DDS (24.38 g, 0.098 mol) and TILCOM TET (6.25 g).

POL.TEEC/TGC.0.TAA

Epon 828 (69.07 g, 0.203 mol), DDS (24.27g, 0.098 mol) and TILCOM TAA (6.66 g).

POL.TEEC.10.TET

Epon 828 (60.81 g, 0.179 mol), TEEC (8.15 g, 0.013 mol), DDS (24.66 g, 0.099 mol) and TILCOM TET (6.25 g). The polymer produced had some cracks on the lower face and was unsuitable for mechanical testing.

POL.TEEC.25.TET

Epon 828 (49.60 g, 0.146 mol), TEEC (19.99 g, 0.033 mol), DDS (24.15 g, 0.097 mol) and TILCOM TET (6.25 g).

POL.TEEC.10.TAA

Epon 828 (60.55 g, 0.178 mol), TEEC (8.11 g, 0.013 mol), DDS (24.55 g, 0.099 mol) and TILCOM TAA (6.66 g). The polymer produced was very brittle and highly fractured on the lower surface, hence unsuitable for mechanical testing.

POL.TEEC.25.TAA

Epon 828 (49.39 g, 0.145 mol), TEEC (19.90 g, 0.032 mol), DDS (24.04 g, 0.097 mol) and TILCOM TAA (6.66 g). The polymer cured before the mixture had

completely degassed (although only a very small amount of bubbling was left) but it was not brittle and cracked on the lower face on this occasion.

Boron trifluoride monoethylamine complex is a catalyst used to ensure complete curing of epoxy resin / DDS systems, although not at a reduced temperature[44]. The following polymers were made using the same method as for POL.TEEC/TGC.0 using Formula 4.1 in the first instance and Formula 4.2 when TEEC was present (recalculating for 100 g total mass). The cure temperature was 177°C in these cases.

POL.TEEC/TGC.0.BF_3

Epon 828 (74 g, 0.218 mol), DDS (26 g, 0.105 mol) and BF_3-MEA (0.76 g, 0.007 mol).

POL.TEEC.10.BF_3

Epon 828 (64.87 g, 0.191 mol), TEEC (8.69 g, 0.014 mol), DDS (26.3 g, 0.106 mol) and BF_3-MEA (0.76 g, 0.007 mol).

POL.TEEC.50.BF_3

Epon 828 (34.08 g, 0.100 mol), TEEC (41.10 g, 0.067 mol), DDS (26.3 g, 0.106 mol) and BF_3-MEA (0.76 g, 0.007 mol). This polymer suffered from almost circular fracture patterns appearing throughout making the panel unsuitable for mechanical testing.

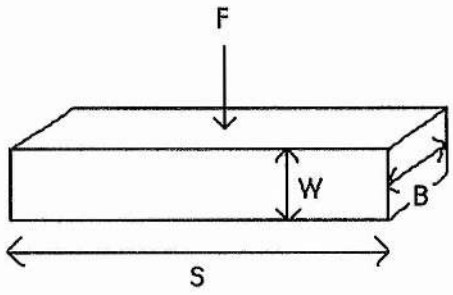
4.3.3 Testing procedures

4.3.3.1 Mechanical testing

Flexural measurements were made using a three-point-bend test on an Instron 6022. Samples were of approximate dimensions 50mm x 10mm x 5mm with accurate

measurement of each individual sample required for the procedure. Fig. 4.56 (below) shows a representation of a sample.

Fig. 4.56



Where F is the force applied

S is the span of the sample between which the force is applied

B is the breadth of the sample

W is the thickness of the sample

and let δ be the displacement of the sample below the horizontal at the point where the force is applied.

Flexural strain, flexural stress and modulus measured by flexure are all automatically calculated by the computer connected to the testing apparatus. Strain and stress are given as maximum values when the sample breaks. Modulus is proportional to the gradient of the graph of stress against strain which, for a thermosetting polymer, is generally only a straight line in the early part of the graph. For this reason it is important to make the modulus measurements at this time. Hence modulus points for the computer calculations were selected in the early part of the graph (0.3 to 1.5 mm of displacement).

For the samples tested here by flexural measurements the stress at break was the same as the maximum stress because the materials were subject to negligible failure before breaking.

The formulae used in the computer programs were as follows:

$$\text{Flexural strain } (\varepsilon) = \frac{6\delta W}{S^2}$$

$$\text{Flexural stress } (\sigma) = \frac{3FS}{2BW^2}$$

$$\text{Modulus} = \frac{\text{stress}}{\text{strain}} = \frac{FS^3}{4B\delta W^3} = \frac{mS^3}{4BW^3}$$

where m = the gradient of the F against δ graph.

Tensile tests were carried out using a tension-up test on an Instron 6022. Samples were of approximate dimensions 100mm x 10mm x 5mm with accurate measurement of each individual sample required for the procedure. Parameters were the same as for the flexural tests above except that the span (S) was measured as the distance between the two points where the sample was clamped and the displacement (δ) was measured as the distance the sample was stretched.

Tensile strain, tensile stress and modulus measured by tension are again all measured and calculated by the computer using the formulae below.

$$\text{Tensile strain } (\varepsilon) = \frac{\delta}{S}$$

$$\text{Tensile stress } (\sigma) = \frac{F}{BW}$$

$$\text{Modulus} = \frac{\text{stress}}{\text{strain}} = \frac{FS}{BW\delta} = \frac{mS}{BW}$$

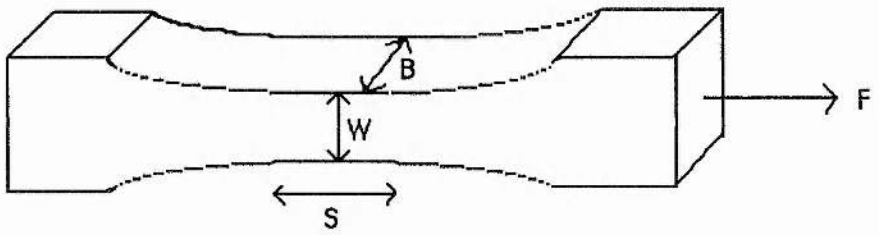
where m = the gradient of the F against δ graph.

Modulus points are again taken from the early part of the stress / strain graph while the line is straight (0.2 to 0.8 mm of displacement).

Tensile strain and tensile stress results cannot be obtained from the regular samples because they tend to break in the jaws of the clamps, not in the middle of the sample. Therefore the maximum value has not been reached, but as long as the second modulus point is reached before this premature breaking the modulus value is unaffected.

Specially machined "dog-bone" samples are required to obtain accurate tensile strain and tensile stress values. These "dog-bone" samples (Fig. 4.57) are narrower in the middle so they will break at this point rather than in the clamp jaws.

Fig. 4.57



Parameters are the same as for the flexural tests above except that the span (S) was measured as the distance between the two extremities where the sample is thinnest and the displacement (δ) was measured as the distance the sample was stretched.

4.3.3.2 Glass transition temperature

Dynamic mechanical thermal analysis (DMTA) was carried out by Messrs I.D. Luscombe and A. Broadhurst of the Thermal Analysis Group in the Characterisation and Measurement Facility, ICI Wilton. A single cantilever mode was applied with test frequency = 10 Hz, strain = x4 and heating from 30°C to above the T_g at a rate of 2°/min in an atmosphere of pure nitrogen. Samples were of approximate dimensions 40mm x 10mm x 5mm.

Differential Scanning Calorimetry (DSC) experiments were carried out using a Perkin-Elmer DSC7 instrument at a heating rate of 10°C min^{-1} in a nitrogen atmosphere on ~5mg samples.

4.3.3.3 Fracture mechanics

Fracture mechanic measurements were carried out by Dr. R. Moore and his staff in the Mechanical and Tribological Properties Workgroup in the Characterisation, Analytical and Polymer Science Group at ICI Wilton. A Linear Elastic Fracture Mechanics (LEFM) analysis was used at a deformation rate of 1mm min^{-1} in air at 23±2°C.

4.3.3.4 Water absorption

Polymers were cut into small pieces of dimensions approximately 10mm x 10mm x 5mm using a diamond edged saw. These pieces were dried in an oven at ~80°C to a constant mass and, once cool, were immersed in water at room temperature. At regular intervals theses samples were blotted dry, so that only the surface water was removed, and weighed and the increase in mass recorded.

At the end of the above experiments the samples were heated in an oven at ~80°C to constant mass.

4.3.3.5 Dielectric measurements

Dielectric measurements were carried out on samples of approximate dimensions 10mm x 10mm x 1mm at the University of Strathclyde by Prof. R.A. Pethrick, Dr. D. Hayward and Dr.J.H. Daly using a "two terminal" type measurement. Further details were not supplied.

SUMMARY

The original aim of this project was to investigate the possibility of synthesising a novel polymer system combining the better properties of cyanate ester resins and epoxy resins. Cyanate ester resins generally have improved resin properties (especially in terms of water absorption, dielectric constant and microcrack resistance) but require higher curing temperatures, which are less economical and introduce residual stresses into the cured polymer. The wide range of applications available for the presently marketed polymers was deemed to make the present study worthwhile.

Three strategies were decided upon in order to achieve the above aim:

1 - To find a cyanate ester that cures at a lower temperature (Chapter 2).

2 - To use mixed epoxy and cyanate ester resins (Chapter 3).

3 - To find a way to design chemically such a polymer from knowledge of the existing ones (Chapter 4).

In Chapter 2 it was revealed that different cyanate esters cure at different temperatures, but that no obvious correlation exists between curing temperature and either steric or electronic effects of the ring substituents. It was also shown that the mixing of two dicyanate esters, one of which cures at a lower temperature than the other, leads to some reduction in the overall curing temperature required, but it was not considered a sufficient enough reduction to warrant further study at this stage.

In Chapter 3 the usefulness of a previously proposed co-reaction between cyanate esters and epoxides, for the purpose of achieving the main aim of this project, was examined. It was discovered that the previous work in this area was full of inconsistencies that put many of the proposed conclusions in doubt. However, further examination of the alleged co-reaction did not clarify the situation. The main information that can be assimilated from all the research carried out in this area is that any co-reaction between cyanate esters and epoxides is unpredictable, can vary significantly with reaction conditions and is in any case a minor reaction pathway by comparison with the self-reactions of the two individual reactants. It was therefore

decided that further pursuit of this strategy was also likely to prove unrewarding in the short term.

In Chapter 4 a study was made into the effects of including novel monomers in a standard epoxy resin system. These novel monomers had a cyanurate backbone with epoxide functionality. Cyanurate ring structures are formed when cyanate esters cure, but, because of the epoxide functionality, these monomers can be cured at the lower temperatures of epoxy resins, and, because of the inclusion of the cyanurate ring structures, it was hoped that the improved properties of cyanate ester resins could be attained. The testing experiments were of a preliminary "scouting" nature, mainly concerned with the observation of trends, so care must be taken in their interpretation. However what was discovered was: in most cases (mechanical, dielectric and water absorption properties) increasing the amount of cyanurate-based monomer into an epoxy resin system improves the properties from those of epoxy resins towards those of cyanate ester resins; in the case of fracture toughness there was no noticeable difference when cyanurate monomer was included; and there appears to be a detrimental effect on the glass transition temperature when the amount of cyanurate is increased. The curing temperature can be varied by the use of different cure catalysts and the precise properties of the polymer can be adjusted by altering the amount of cyanurate-based monomer included. This means that, if the T_g problem can be overcome or a high T_g is not required, this type of polymer could be used for many applications, either for improved properties in those where epoxy resins are currently employed, or for greater economy in those where cyanate ester resins are currently preferred.

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